

<http://researchcommons.waikato.ac.nz/>

## **Research Commons at the University of Waikato**

### **Copyright Statement:**

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

The thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of the thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from the thesis.

**Surface Roughening of Platinum Wire**  
**An Electrochemical and Mechanical Approach**

A thesis

Submitted in fulfilment

of the requirements for the degree

of

Masters of Engineering

at

**The University of Waikato**

by

**Stefan M. Gyga**



THE UNIVERSITY OF  
**WAIKATO**  
*Te Whare Wānanga o Waikato*

**University of Waikato**

2017

## Abstract

In order to make implanted electrodes MRI safe several methods have been explored. One of those methods involves increasing AC resistance by roughening the surface of the implanted platinum wires. This thesis explores an electrochemical and a mechanical approach to reliably induce 15 micro meter deep surface defects. The electrochemical approach dissolves the outermost layer of the wire and redeposits a porous layer on the surface that does not grow more than 2 micro meters thick. It is predicted that this layer may be grown to desired thickness if the source of platinum comes from within the solution treatment takes place in rather than the treated wire itself. The mechanical approach induces fatigue cracks that grow predictably and can be controlled to desired size. The limitations are the small amount of wire that may be treated at a time through rotational fatiguing, and the initial quality of the treated wire. High quality wire and an ultrasonic fatigue setup may remedy these limitations.

## Acknowledgements

Firstly I would like to thank Professor Jonathan Scott for making this research possible. His contagious enthusiasm motivated me throughout the project. Thank you for giving me the freedom to explore different avenues while still being there to give feedback and nudge me in the right direction when I met difficulty.

I would like to thank Saluda Medical who provided the blueprints for the initial electrochemical approach.

Thank you to Helen Turner for helping me with the electron microscopy and in gathering the micrographs that were used throughout this study.

Thank you to Dirk Hartung for giving me context and insight into the implant more broadly.

Thank you to Melissa Gygax, Massimo Gygax, and Louise Kong for funding my studies.

Last but not least, a big thank you to the people in the University of Waikato Large Scale Laboratory and DG12 room. All of you were very helpful from organising room to work in to building test rigs with me.

## List of Figures

Figure 1 - Untreated Platinum Wire, 800x magnification.....	3
Figure 2- Platinum wire resistance measurements .....	5
Figure 3 - Otteniser pulse shape .....	11
Figure 4 - Platinum surface, 1 KHz treatment.....	12
Figure 5- Platinum surface, 500Hz treatment showing the different orientations of the growth.....	13
Figure 6-Grain boundaries on untreated platinum wire.....	14
Figure 7- A test to show the corrosion of grain boundaries in platinum wire.....	14
Figure 8- Ottenised platinum wire at 190mA .....	15
Figure 9 – Cross section of a treated wire showing internal cracking .....	18
Figure 10 – Resin with imbedded platinum wire samples.....	19
Figure 11 - Deformation from cutting a wire with scissors.....	20
Figure 12- Platinum deposition micrograph taken from Fumihiko Koderu 2007 .....	21
Figure 13- Platinum deposition micrographs from Ottenisation.....	21
Figure 14-Surface of an Ottenised platinum wire.....	22
Figure 15 - Ottenised platinum wire showing deposited layer thickness.....	23
Figure 16- Typical stress-strain behaviour of a ductile material.....	24
Figure 17- Cyclical fatigue loading .....	25
Figure 18 - Stress-strain behaviour of platinum derived from Koh et.al. experiments ....	26
Figure 19 - Unit cell of an FCC material.....	27
Figure 20 - <110> slip directions .....	28
Figure 21- Model illustrating one form of dislocation movement (edge dislocation).....	28
Figure 22 - Micrograph of a micro crack in copper.....	30
Figure 23- Slip bands formed in a fatigued copper sample .....	30

Figure 24- 5,000 fatigue cycle platinum sample showing crack initiation. 1.5 micron was the largest crack found .....	31
Figure 25- Typical behaviour of fatigue cracking. Log-log plot .....	32
Figure 26- Ductile failure of a fatigued platinum wire sample .....	33
Figure 27 - Model of stress at crack tip in the copper wire .....	34
Figure 28 - Crack tip depth for copper at 0.5% strain cycles .....	35
Figure 29- Crack tip depth for platinum at 0.5% strain cycles .....	36
Figure 30- Drill chuck stand for mounting onto a DC motor, design and the printed part .....	38
Figure 31- Stand to hold a wire in a constant bend.....	39
Figure 32- Test fixture when assembled.....	40
Figure 33 - Copper wire before (left) and after (right) fatigue .....	41
Figure 34- Copper surface after fatigue to failure .....	41
Figure 35- Platinum surface of a sample fatigued to failure .....	42
Figure 36- Example of cracks used for size analysis.....	43
Figure 37- Single large crack in 20,000 cycle sample .....	44
Figure 38- Cross section of a crack in a 20,000 cycle fatigue platinum wire .....	44
Figure 39 - Experimental data plotted on the crack growth model .....	45
Figure 40 - Statistical interpretation of crack density.....	47
Figure 41 - Pure pitting at the surface of a platinum wire.....	52
Figure 42- Cross section of a pitted platinum wire sample .....	53

## Contents

Introduction .....	1
Thesis Objectives.....	2
Platinum Wire .....	2
Skin effect .....	5
1. Ottenisation .....	6
1.1. Background .....	6
1.2. Corrosion.....	7
1.3. Deposition .....	8
1.4. Ottenisation Process .....	8
1.5. Otteniser .....	9
1.5.1. Program.....	9
1.6. Setup and Preparation .....	9
1.6.1. Electric Pulse .....	10
1.6.2. Pulse Duration.....	12
1.6.3. Pulse Magnitude .....	15
1.7. Treatment Duration .....	16
1.8. Hydroxide Reduction.....	16
1.9. Ottenisation Results.....	17
1.9.1. Corrosion.....	17
1.9.2. Deposition.....	18
1.9.3. Size and Shape .....	20
1.9.4. Depth of Treatment .....	22
2. Mechanical Fatigue .....	23
2.1. Background .....	24
2.2. Mechanical Properties .....	25

2.3.	FCC Materials .....	26
2.4.	Fatigue Mechanics .....	29
2.4.1.	Crack Initiation .....	29
2.4.2.	Crack Propagation .....	31
2.4.3.	Failure .....	32
2.5.	Mathematical Model .....	33
2.6.	Experimental Setup.....	36
2.7.	Rotational Fatigue.....	37
2.8.	Test Rig Design .....	37
2.9.	Results, Copper .....	40
2.10.	Results, Platinum .....	42
3.	Discussion of Results.....	45
3.1.	Oxygenation .....	46
3.2.	Mechanical Fatigue .....	46
	References .....	49
	Appendix A Current Density Calculation.....	51
	Appendix B Pure Pitting of Platinum Wire.....	52



## Introduction

Implanted electrodes are a useful and powerful tool in the biomedical industry. The advance of different types of stimulators has led to the widespread use of implants. This has led to a demand for improvements in designs. One of the limitations is the danger posed when an implant patient undergoes nuclear magnetic resonance imaging (MRI).

The strong RF field that the MRI machine generates deposits energy into implanted electrodes. This leads to a local increase in temperature large enough to cause tissue damage. In order to combat this limitation several different methods are being researched and tested. One of the possible improvements is to increase the AC resistance of the implanted wires.

This increased AC resistance would impede the induced current from flowing, resulting in less deposited energy. In order to maintain a low power system to preserve battery life, implants need the DC resistance of the leads to be low. To stop the RF fields from causing heating and harm a way to increase the AC current impedance while preserving DC conductivity is needed. While this is not viable at low AC frequencies, the high operating frequency of MRI machines allows the possibility to take advantage of the skin effect.

The skin effect is the tendency of AC current to flow along the surface of the conducting medium. In order to increase AC resistivity the research done herein studies methods to roughen thin conducting wire surface of platinum, a biocompatible material. The type of roughening sought is a surface modification that penetrates deep enough to impede AC current while maintaining a solid, low defect dense core to preserve DC conductivity.

## Thesis Objectives

The Objective of this paper is to look at different methods to increase the surface roughness of thin wires. To achieve this goal, two primary methods were studied. The first was an electrochemical process that aims to grow a porous layer on the surface of the wire. The process used was one developed by Josephus M. Otten and modified to fit the needs here.

The second method was controlled fatiguing of the wire. Fatigue is a very well-studied phenomenon because of the effects it has on structures and mechanical components. The final goal of these methods is to be able to control the depth and density of surface defects in for later study of skin effect on the system. The final goal of the roughening methods is for application on 100 micron thick platinum wire.

## Platinum Wire

The wire used in the studied electrodes is made of platinum. Platinum is a metal that is both biocompatible and resistant to corrosion. In addition, it is a malleable metal that is resistant to fracture and can bend to the movements of the implanted patient.

The platinum wire studied was provided by California Fine Wire. It is listed as a 90% platinum 10% iridium wire that is drawn to a thickness of 100 $\mu$ m. The wire properties that are listed with the product are below.

90% Platinum, 10% Iridium	
Specific Resistivity ( $\mu\Omega$ -cm <sup>2</sup> /cm)	24.94
Density (lbs/in <sup>3</sup> )	0.778
Melting Point (C )	1775

*Table 1 - Platinum Wire Properties*

The resistivity of the wire is listed as  $2.494 \times 10^{-9} \Omega \text{ m}^{(1)}$ . However, measured results were significantly different. The measured resistivity of the wire was  $2.2 \times 10^{-7} \Omega \text{ m}$  given by

$$\rho = R \times \frac{A}{l}$$

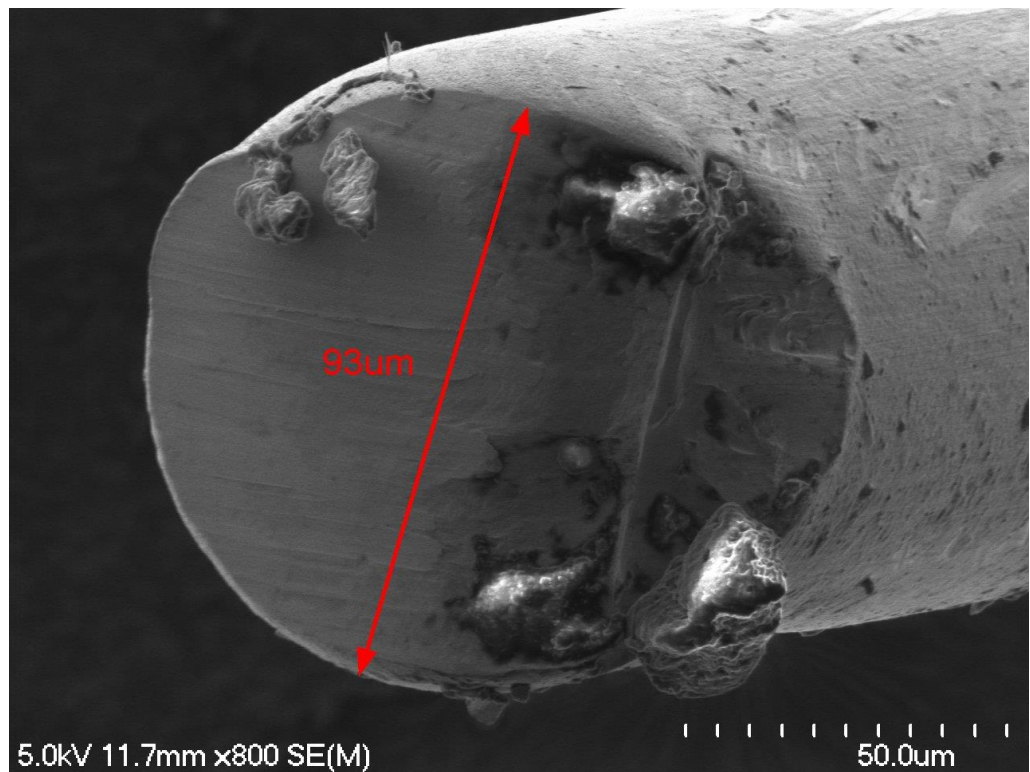
Where

R: resistance of the sample

A: cross-sectional area

l: length of the sample

The real cross sectional area was measured by using a calibrated micrograph of a sample of the wire. An untreated sample of the wire was analysed using ImageJ, an image processing program.



*Figure 1 - Untreated Platinum Wire, 800x magnification*

The final diameter of the wire was measured at 93 micrometres. This gives a cross sectional area of:

$$A = 6.8 \times 10^{-9} \text{ m}^2$$

After the resistance was measured, as shown in table 2, the resistivity was calculated and averaged. The resistivity under 10cm (0.1m) was excluded from the final result because of uncertainty from measurement as can be seen from the graphed resistivity (figure 2).

wire length (m)	resistance (Ohm)	resistance (Ohm)
0.01	0.6	0.9
0.02	0.9	1.1
0.03	1.3	1.2
0.04	1.7	1.5
0.05	2	1.8
0.06	2.3	2
0.07	2.7	2.3
0.08	3	2.5
0.09	3.2	2.8
0.1	3.5	3.3
0.11	3.9	3.6
0.12	4.2	3.9
0.13	4.4	4.1
0.14	4.7	4.5
0.15	5	4.8
0.16	5.2	5.2
0.17	5.6	5.5
0.18	6	6
0.19	6.3	6.2
0.2	6.5	6.5

*Table 2- Platinum wire resistance measurements*

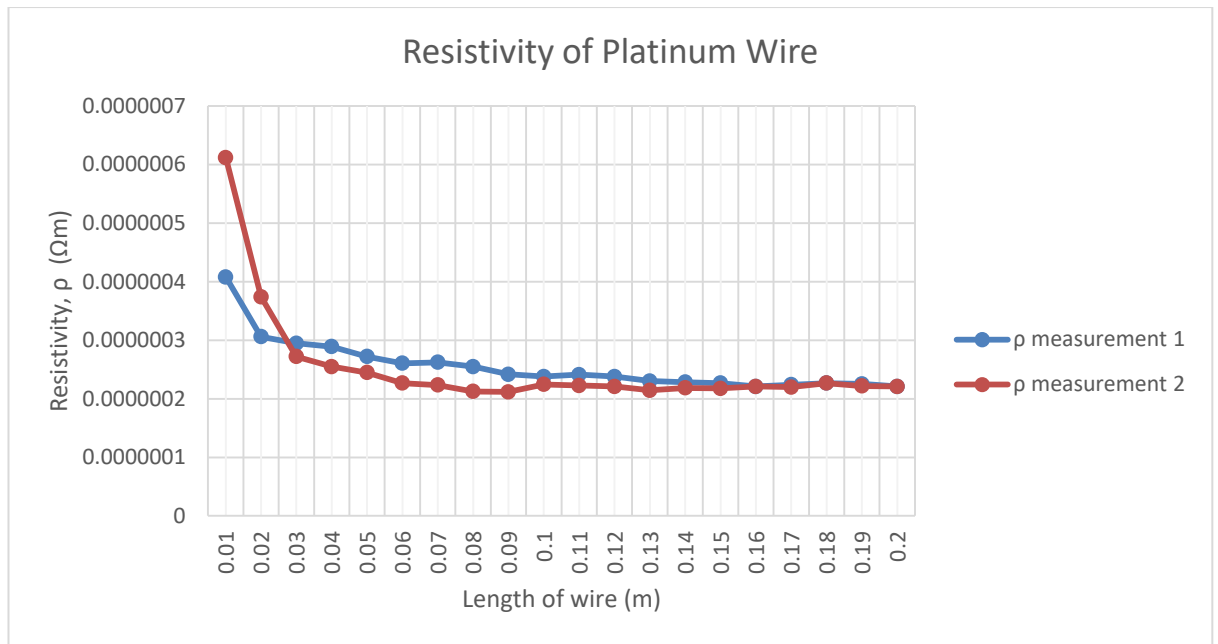


Figure 2- Platinum wire resistance measurements

## Skin effect

The skin effect is a measureable phenomenon that describes how the current flows within a solid conductor. The higher the frequency, the more the current flows along the surface of the wire. In order to know how deep the surface defects need to penetrate, the depth of current flow needs to be estimated. The extent of the skin effect is related to:

f: the frequency

ρ: the resistivity of the material

μ: the absolute magnetic permeability of the material

The skin effect,  $\delta$ , is given by

$$\delta = \sqrt{\frac{\rho}{\pi \times f \times \mu}}$$

The absolute magnetic permeability is listed as  $1.25697 \times 10^{-6}^{(2)}$ . The frequency used is the typical operating frequency of an MRI machine is 128MHz but newer machines will increase this frequency to 300 MHz<sup>(3)</sup>. This means that

the current flows in a surface layer 15 microns deep. Therefore, the surface defects need to penetrate about that deep into the platinum wire.

## **1. Ottenisation**

The first approach was to try and adapt a method that was researched by Josephus M. Otten. This method has been called “Ottenisation” and is an electrochemical treatment that was originally designed to increase surface area for cochlea implants. The basic mechanics of this method apply electrochemical dissolution and deposition to modify surface morphology.

### **1.1. Background**

In order to understand the Ottenisation process, an understanding of electrochemistry is necessary. When a periodic perturbing potential is applied to a face centred cubic (FCC) metal such as platinum, a deposited layer of metal can be grown to increase surface roughness. The textures are dependent on the positive and negative pulse intensities and the frequency<sup>(4)</sup>.

This growth on the surface is a result of electrochemical dissolution and electrochemical deposition. This process uses the platinum metal dissolved into solution during the electrochemical dissolution as the material for the deposition. This allows for surface modification with minimal loss of mass and negligible loss of cross sectional area. The parameters to optimise surface roughening are dependent on the corrosion and deposition steps of the process.

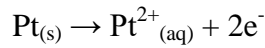
There are several possible reactions that occur in this system when bias is applied. Below is a list of the platinum reactions along with their standard reduction potentials vs. a standard hydrogen electrode<sup>(5)</sup>.

Reaction	E <sup>0</sup> /SHE
$\text{Pt}^{2+} + 2\text{e}^- \leftrightarrow \text{Pt}$	1.19V
$\text{PtOH}^+ + \text{H}^+ + 2\text{e}^- \leftrightarrow \text{Pt} + \text{H}_2\text{O}$	1.2V
$\text{Pt}(\text{OH})_2 + 2\text{e}^- \leftrightarrow \text{Pt} + 2 \text{OH}^-$	0.14V
$\text{PtO}_2 + 2 \text{H}^+ + 2\text{e}^- \leftrightarrow \text{PtO} + \text{H}_2\text{O}$	1.01V
$\text{PtO}_2 + 4 \text{H}^+ + 4\text{e}^- \leftrightarrow \text{Pt} + 2 \text{H}_2\text{O}$	1.00V
$\text{PtO}_3 + 4 \text{H}^+ + 2\text{e}^- \leftrightarrow \text{Pt}(\text{OH})_2^{2+} + \text{H}_2\text{O}$	1.5V
$\text{PtO}_3 + 2 \text{H}^+ + 2\text{e}^- \leftrightarrow \text{PtO}_2 + \text{H}_2\text{O}$	1.7V

*Table 3 - Possible platinum reactions and their potentials*

## 1.2. Corrosion

The first step in the Ottenisation process is the dissolution step. This can be modelled as a basic electrochemical corrosion. The platinum is attached to a positive bias while submerged in a salt bath. This takes electrons out of the metal and pushes platinum ions out.



In order to ensure that the platinum is properly ionized, the applied potential has to be greater than the reduction potential of 1.19V vs. SHE. This ensures that platinum ions that are expelled into the solution. Using a potential greater than the oxidation potential of Pt also causes combination with other ions within the salt bath to form hydroxides and other oxides.

During the corrosion step, PtOH, Pt(OH)<sub>2</sub>, PtO, and PtO<sub>2</sub> are formed. There is a possibility of PtO<sub>3</sub> forming depending on the potential used. These products are expelled into solution and is evidenced by the formation of hydrogen gas, H<sub>2(g)</sub>. This gas takes the form of bubbles that float to the surface.

The short duration of the corrosion step during the full Ottenisation process causes high energy areas to corrode preferentially. These high energy areas include the grain boundaries, physical defects, and inclusions present along the surface.

### 1.3. Deposition

The second phase of the Ottenisation process is depositing the dissolved platinum and its ions back onto the substrate. To achieve this, a negative bias is applied. This causes an excess of electrons to be put into the system. This pulls the dissolved platinum back onto the surface of the wire and reduces the oxides and hydroxides.

In order to reduce and redeposit the platinum, a bias of the same magnitude as the oxidation bias needs to be applied. This allows all the different platinum species to be reduced. There is still the possibility that some of the platinum is left in solution due to different kinetic effects, however the loss has been observed to be minimal.

### 1.4. Ottenisation Process

As a whole, Ottenisation is a method that optimises and streamlines the oxidation/reduction of the platinum. The original intent of the process was to reduce pacing polarization of a platinum electrode by increasing surface area through roughening. For the purposes of this study, the process is modified to penetrate deeply into the wire as opposed to just looking at surface roughness.

This deep, roughened structure can be used to increase impedance of high frequency AC currents if the layer is thick enough. In order to modify the procedure to fit this purpose, a starting point of this research was the patent filed by J.M. Otten.

The original patent for Ottenisation was filed October 15, 1992. The patent was given on July 5 1994 and is patent number 5,326,448. This patent outlines parameters to modify the surface of electrodes. These parameters are given as upper and lower bounds for each variable, so testing and some modification had to be carried out.



## 1.5. Otteniser

In order to apply the oscillating current, a device had to be built and programmed to output the desired currents. The device used was built around an Arduino board. This allowed for control over the output pulse durations and currents as well as being able to receive and record real time data.

The inputs required to run this device are a standard 220V, 50Hz and a 100V, stepped down current from a Variac transformer. In addition a USB connection to a computer that runs software that controls the device is also needed.

### 1.5.1. Program

In order to run the Otteniser a few, small modifications were made to the program written for the Otteniser. This program is written in Arduino Software (IDE) and is controlled by a GUI written in Python. Modifications were made to allow the device to connect to my Windows 10 computer. Other minor changes were made to functions calling for files in directories that differed between the author's system and my own.

## 1.6. Setup and Preparation

After all the power inputs and computer are attached to the Otteniser, the output leads are attached to a platinum wire sample, and a titanium counter electrode. The platinum sample is first cleaned in an acetone and isopropyl alcohol in order to remove any contaminants such as oils and dust. This is an important step because the presence of any coating impedes the corrosion and deposition process. This also removes contaminants from being trapped between the solid wire and deposited layer. The platinum electrode and counter electrode are then placed into a salt bath.

This entire process is done in a sodium sulphate solution in order to promote the formation of  $\text{Pt}^{2+}$  ions into the solution<sup>(6)</sup>. Sodium Chloride (table salt) was

not used because it has been observed that presence of  $\text{Cl}^-$  ions cause the platinum to anodically dissolve into  $\text{PtCl}_4^{2-}$  or  $\text{PtCl}_6^{2-}$  <sup>(7)</sup>. Removing the possibility of platinum chlorides forming limits the types of impurities that may form and simplifies the reduction.

A 0.5 molar solution of sodium was sulphate used

$$\frac{142.04g \text{ Na}_2\text{SO}_4}{1 \text{ mol Na}_2\text{SO}_4}$$

The  $\text{Na}_2\text{SO}_4$ , when dissolved, dissociates.

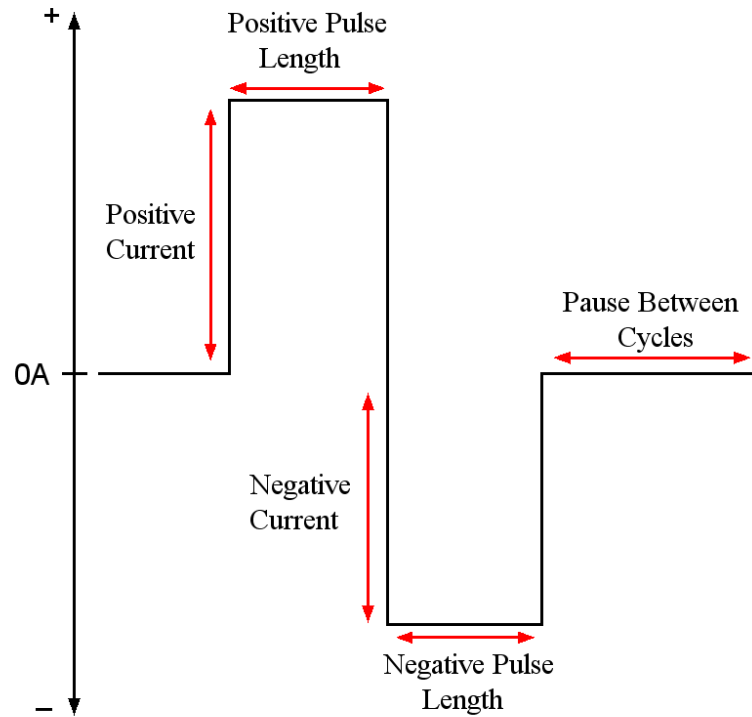


The sodium sulphate solution is constantly sonicated during the process. This is to help dissolve the platinum ions expelled during to process to ensure that there is not localised growth. An even distribution of platinum is desired along the entire surface of the wire. It should be noted that sonication does raise the temperature of the system from 21°C to 33°C. The effects of this rise in temperature have not been extensively studied. Theoretically this small rise in temperature has little effect on the Ottenisation procedure.

The next point of consideration is the applied current to the system. The patent has a large window of operation. It states that the applied amplitudes can range from “1 miliampere to several amperes” <sup>(8)</sup>.

### 1.6.1. Electric Pulse

The largest variable in the treatment of the platinum wire is the applied electric current. The applied electric pulses are square waves with a pause between pulse cycles. The pause allows the deposited material to stabilize and any ions that are left over in the solution to diffuse evenly. The general shape is shown below.



*Figure 3 - Otteniser pulse shape*

The Otteniser allows for parameters to be set for all of the pulse durations and magnitudes by using the GUI.

I\_1: Positive current

I\_2: Negative current

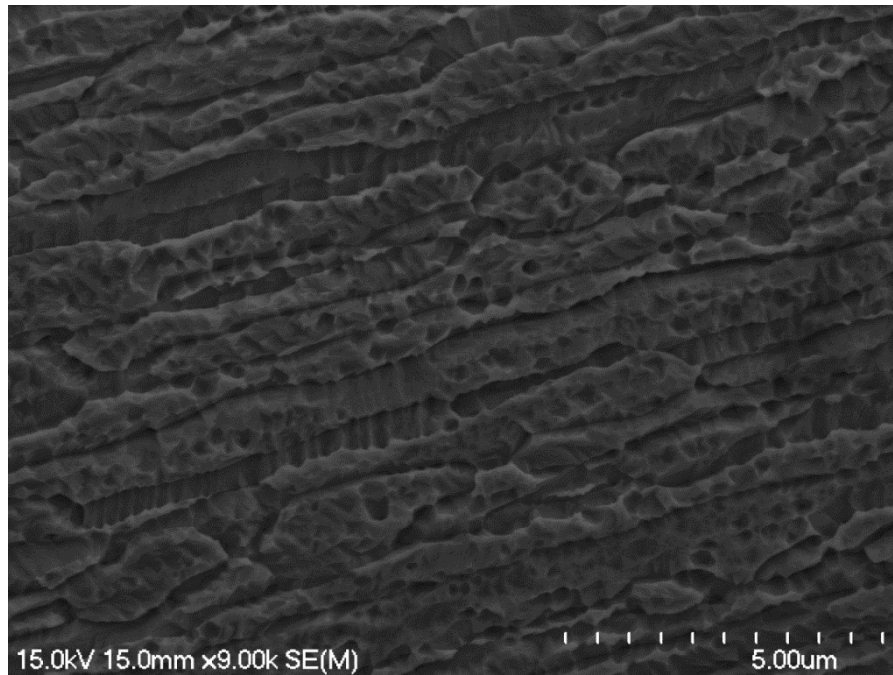
t\_1: Positive pulse duration

t\_2: Negative pulse duration

t\_3: Duration of the pause between cycles

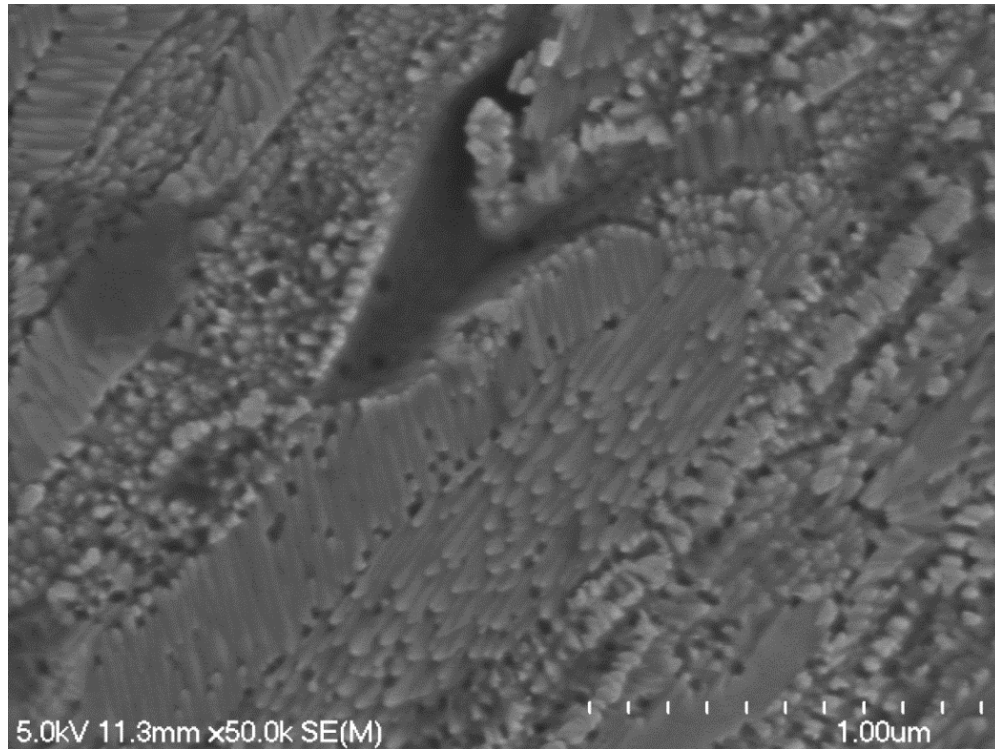
### 1.6.2. Pulse Duration

It has been shown that a frequency of about 1 kHz gives the most desirable surface texture<sup>(4)</sup>. To that end, a set of tests was carried out to determine suitable pulse duration. Tests at frequencies of 1 kHz showed that the corrosion step was not long enough and that the corrosion was shallow and resulted in a rough surface and a shallow treatment.



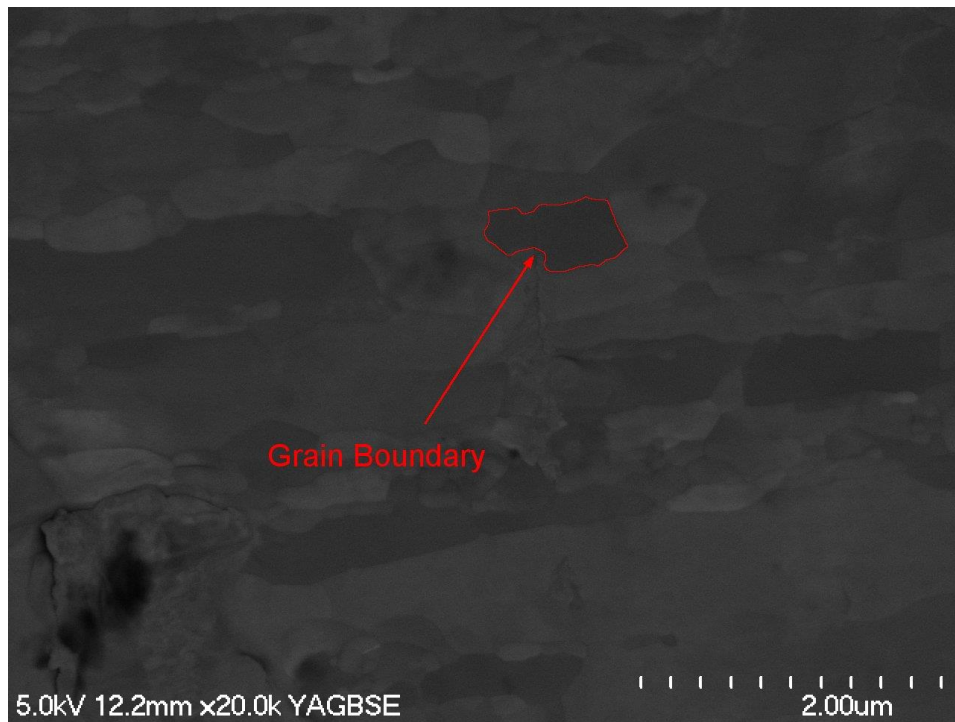
*Figure 4 - Platinum surface, 1 KHz treatment*

When the frequency was turned below 500Hz, the corrosion was deeper but the growth on the surface was textured in an undesirable way. The growth followed the crystallographic orientation of the substrate grain.



*Figure 5- Platinum surface, 500Hz treatment showing the different orientations of the growth*

In the end, a frequency of 704.2 Hz was chosen which translates to positive and negative pulse duration each of 0.71ms. At this frequency, corrosion was deeper than the high frequency tests and followed the grain boundaries. The deposition also resulted in a desirable porous structure. A test that was stopped before the surface was fully modified clearly shows the corrosion along grain boundaries. This shows the preferential corrosion paths illustrated by figures 6 and 7.



*Figure 6-Grain boundaries on untreated platinum wire*



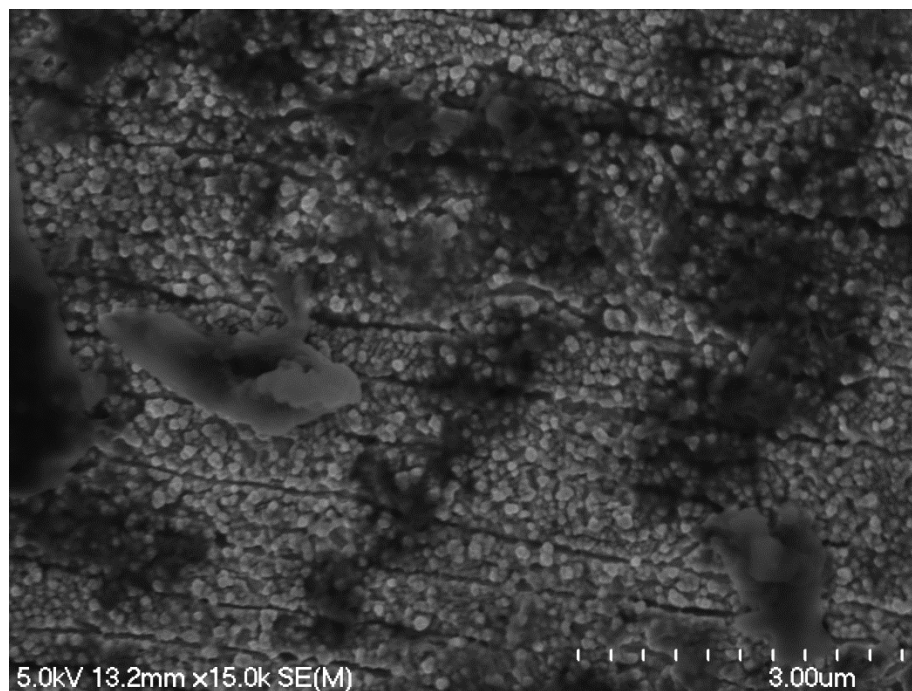
*Figure 7- A test to show the corrosion of grain boundaries in platinum wire*



### 1.6.3. Pulse Magnitude

The next point to be considered was the magnitude of each pulse. A current of 190mA was calculated. A start point was calculated by estimating the current needed to ionise an atomic monolayer of a sample. The assumptions made were that the wire was pure platinum with fully face centred cubic structure (FCC). A full derivation can be found in Appendix A.

When 190mA was used, the deposited material was porous and looked fine, however, the depth of treatment was limited. A picture below shows the favourable porous morphology, but the underlying corrosion grain boundary corrosion crevices can still be seen in some places, suggesting that the treatment depth was limited.



*Figure 8- Ottenised platinum wire at 190mA*

This may have been corrected by longer treatment times. Another way, which was chosen instead, is to increase the current magnitude to 250mA. This kept the porous surface, decreased needed treatment duration, and resulted in the maximum depth of treatment. Another apparent advantage of increasing current

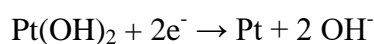
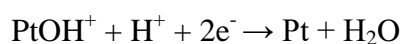
magnitudes instead of increasing treatment time is the decrease in loss of material. This, however, was not studied in depth.

## 1.7. Treatment Duration

The duration of the treatment had to be long enough to maximise the thickness of the porous layer deposited on the wire, but not longer. After maximum thickness is reached, further treatment causes loss of mass in the wire because the corroded material is not redeposited with 100% efficiency. The treatment time that has been determined to be appropriate for treatment to a maximum treatment depth is between 450 and 500 seconds.

## 1.8. Hydroxide Reduction

After the Ottenisation treatment, the wire has to undergo a hydroxide reduction step. The deposited platinum contains some hydroxides and these must be removed in order to return to a pure platinum surface.



The study by Visintin concluded using XPS data that the deposited material had an outermost layer that consists mostly of  $\text{Pt}(\text{OH})_4$  and  $\text{Pt}(\text{OH})_6^{2-}$ <sup>(4)</sup>. This was partially confirmed by the presence of hydroxides using energy-dispersive X-ray Spectroscopy (EDS) during scanning electron microscope (SEM) imaging of un-reduced samples. Determining the abundance and type of hydroxides was not pursued since the hydroxides were eliminated after a hydroxide reduction step.



The hydroxide reduction process is done in the sodium sulphate solution and requires a titanium return electrode. The potential between the platinum wire and the return electrode is measured every 5 minutes in order to determine when the process is finished. A reduction potential of 13V is applied to the system while measuring the actual voltage across the cell.

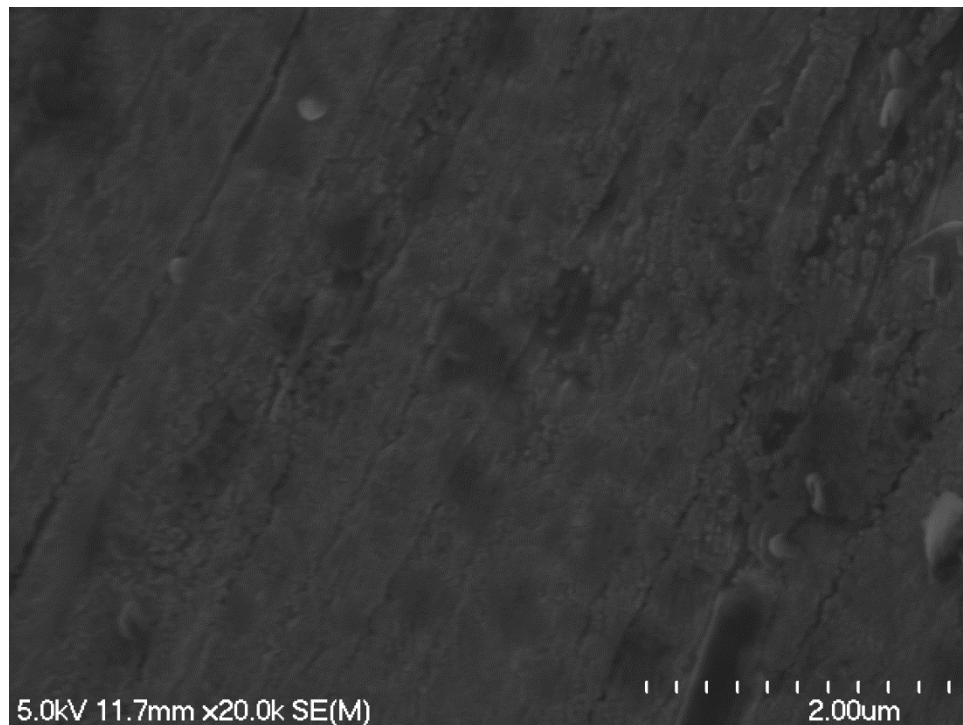
The initial measured potential across the cell varies with the size of the wire that is submerged. After the readings stabilize, which is when the measured potential remains within 10mV (+/- 5mV) for 3 readings (15 minutes), the system is considered to be in equilibrium and complete.

## **1.9. Ottenisation Results**

There was a variety of different tests that were performed in order to reach a set of parameters that yielded the formation of porous platinum at the largest thickness. Outlined in this section are the results of the finalised set of parameters. The different tests and their results have been briefly mentioned earlier in this paper. It should be noted that the tests done were consistently on 10cm long wires. A longer wire has not been treated due to cost and time. A more comprehensive study of the effects of the amount of surface area on the treatment procedure should be conducted in the future.

### **1.9.1. Corrosion**

The corrosion step worked as expected and mirrored regular galvanic corrosion. This means that the corrosion preferentially attacked the high energy facets but also corroded the other faces as well. Along with the typical galvanic corrosion, there was evidence of blistering in the platinum wire. This damage can be seen as deep as 10 microns deep inside the wire.



*Figure 9 – Cross section of a treated wire showing internal cracking*

Blistering is an effect of the large amount of hydrogen gas that is evolved during the Ottenisation process. Some of the hydrogen gas migrates into the corroded material instead of being expelled out into the electrolyte solution. This hydrogen gas builds up and creates voids and internal cracks within the wire. These blisters are unseen from the surface and mechanically weaken the material by reducing the effective cross sectional area.

### **1.9.2. Deposition**

The deposited material formed a porous platinum coating. In order to measure the size, shape, and depth of the treatment, a scanning electron microscope, SEM, was used. In addition, a cross sectional view of the wire needed to be taken in order to determine the depth of treatment and any other sub surface textures that were formed during Ottenisation.

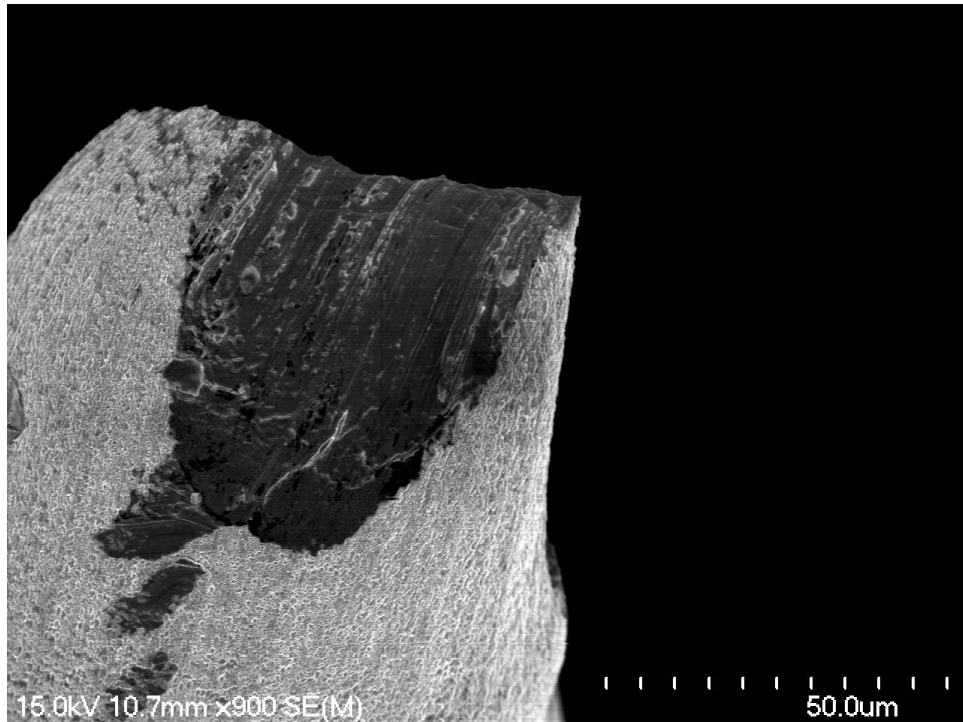
In order to view a cross section of such a small and soft wire, cutting the wire with wire cutters or scissors destroys textures and deforms the wire (figure

11). To get a clean cross section of the wire two different methods were used. The first was to fix the wire in a resin that hardens and then use increasingly higher grit sand paper to eventually diamond paste to whittle down the wire until a clean cross section can be seen.



*Figure 10 – Resin with imbedded platinum wire samples*

The second method is to mechanically fracture the wire by deformation. The fracture requires clamp points in order to initiate the deformation. The clamp points flatten the texture that is formed on the surface. This suggests that the growths are fragile and susceptible to mechanical wear and tear.



*Figure 11 - Deformation from cutting a wire with scissors*

The samples embedded into the resin required a coating of platinum to be imaged in the SEM. This layer made discerning between the porous coat and the substrate difficult. The fractured sample had enough undamaged edge to analyse, and therefore were used more often.

### **1.9.3. Size and Shape**

The microstructure of the resulting product reflects the structure that is found deposited on the counter electrode in regular electrochemical corrosion of platinum in sulphuric acid <sup>(6)</sup> .

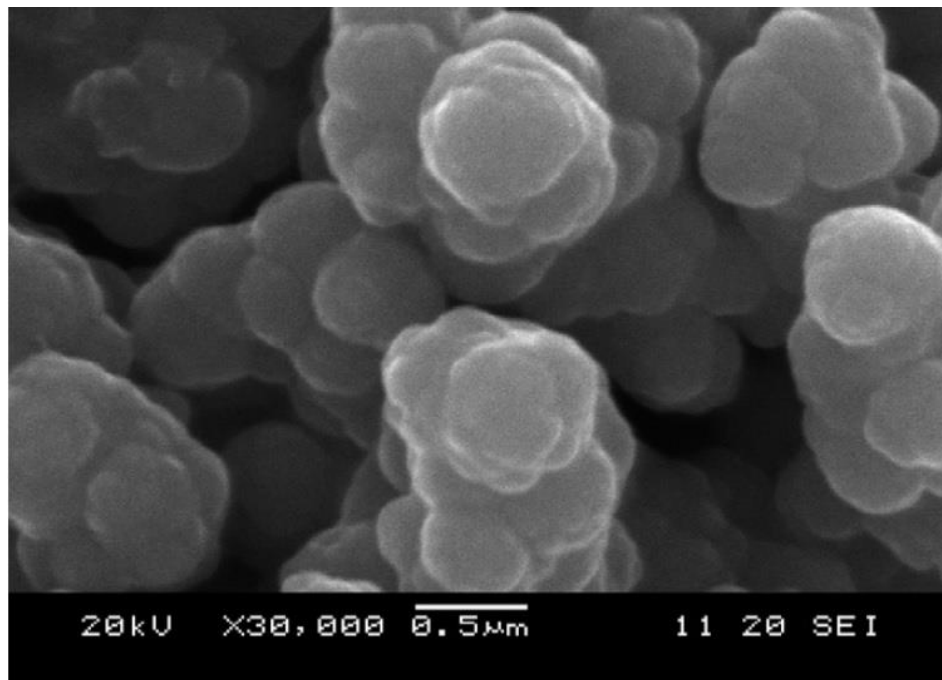


Figure 12- Platinum deposition micrograph taken from Fumihiro Kodero 2007

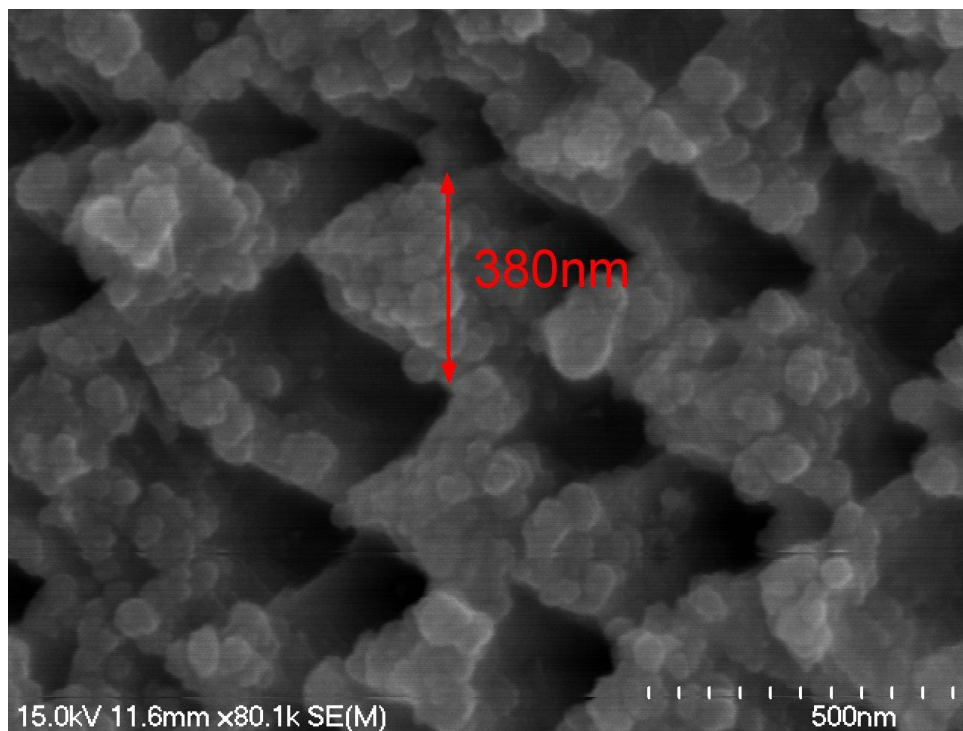
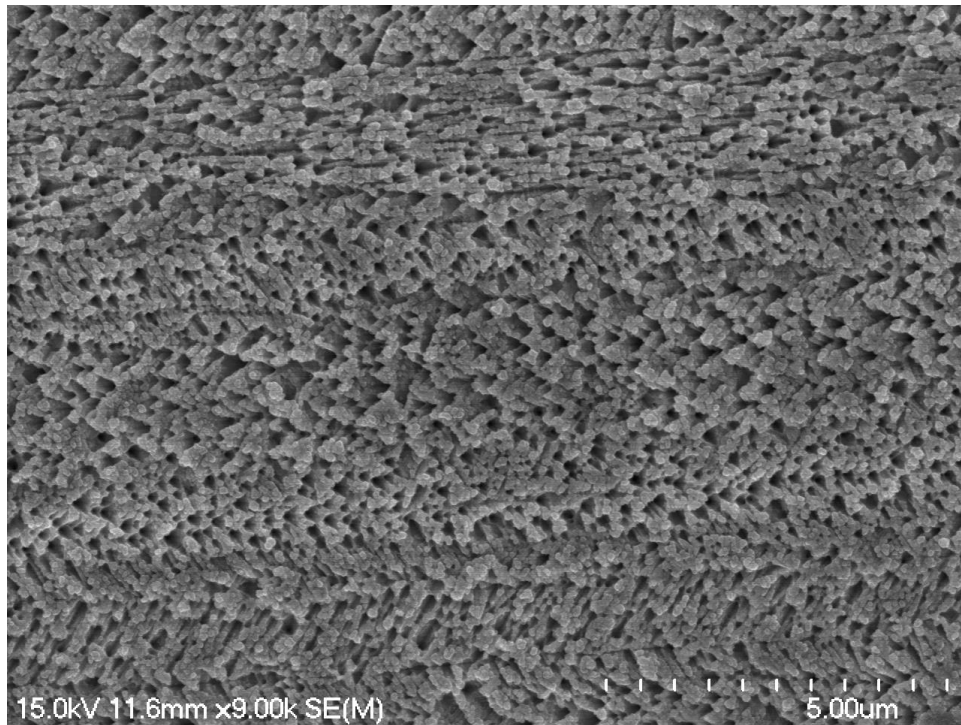


Figure 13- Platinum deposition micrographs from Ottenisation



The coating deposited is symmetrical and repeats predictably along the entire surface of the treated wire.



*Figure 14-Surface of an Oxidised platinum wire*

#### **1.9.4. Depth of Treatment**

The treatment depth reached a maximum value of about 1.5 micro meters. This depth did not increase even after increasing treatment times. In order to measure this, getting a clear cross section was the most challenging part. A clean fractured surface was the clearest view of the treatment depth. This did come with some drawbacks. Firstly, the wire exhibits ductile fracture. This means that only the part where the fracture begins has a clean edge to image.

Secondly, the wire had to be held firmly in order to be fractured. This caused the surface to be flattened as can be seen. This means that the 1.5 micro meter depth might actually be slightly more if the flattened surface texture is taken into account.



*Figure 15 - Ottenised platinum wire showing deposited layer thickness*

## **2. Mechanical Fatigue**

In order to create defects that penetrate more deeply into the surface of the platinum wire, a method to introduce cracks was researched. The method chosen was fatigue cracking. This is because it causes surface roughening due to dislocation accumulation and creates a relatively high density of cracks. In addition, the crack depth can be theoretically controlled to an extent before fracture. The challenges associated with this method of surface modification include controlling crack depth in practice and designing a method to fatigue such a small filament.

## 2.1. Background

Fatigue cracking is a type of fracture that involves applying a repeating stress to a material. The types of stress applied can be categorised into two regimes of fatigue life: low cycle fatigue and high cycle fatigue. The low cycle fatigue applies a stress that is greater than the yield strength of the material. This type is considered strain controlled and typically fails below  $10^4$  stress cycles. The high cycle fatigue regime fails at a higher number of cycles while applying a much less than the yield strength.

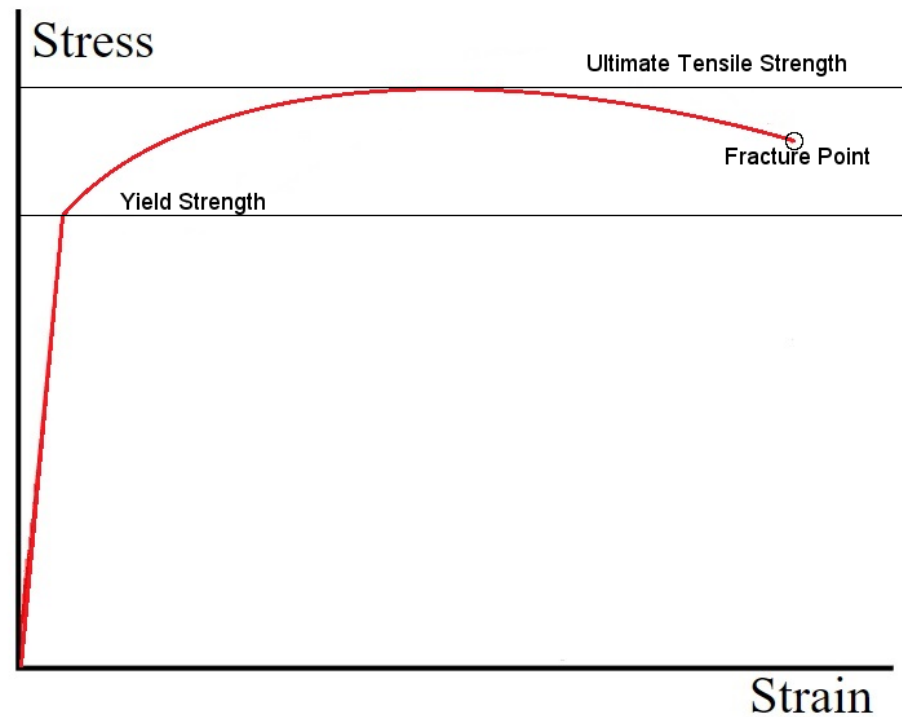


Figure 16- Typical stress-strain behaviour of a ductile material





*Figure 17- Cyclical fatigue loading*

In order to understand the mechanics of fatigue cracking, the mechanical properties have to be taken into account. In addition, the small size of the sample is a very important consideration. The 100 micron thick wire sample was too small to test mechanically with available equipment so the theory and modelling was done using pre-established typical values for materials used taken from a book on Fracture Mechanics <sup>(9)</sup> and various published studies.

## **2.2. Mechanical Properties**

Platinum is a ductile material. It has a stress/strain curve shape that shows a large plastic region after the elastic region. Unfortunately, the wire was too thin to be able to conduct tensile tests on it with the available equipment. However, some approximate figures are available. The datasheet from California Fine Wire sites an ultimate tensile strength (UTS) of 380-830 MPa <sup>(1)</sup>.

This UTS is extremely high and atypical for platinum. Other suppliers list platinum and platinum wires as having a UTS of 120-300 MPa <sup>(10) (11) (12)</sup>. In order to remain within the high cycle fatigue regime, an applied stress of less than the

yield strength has to be applied. California Fine Wire does not list yield strength for their material, however other manufactures list platinum with yield strength between 30 and 200 MPa depending on the manufacturing method. From the data available on manufacturing methods it is safe to assume that the yield strength is above 75 MPa. This was later confirmed by tests of greater than  $10^4$  cycles of under 50 MPa before fracture. A tensile test done by S.J.A. Koh<sup>(13)</sup> shows the stress-strain behaviour of platinum in the elastic region.

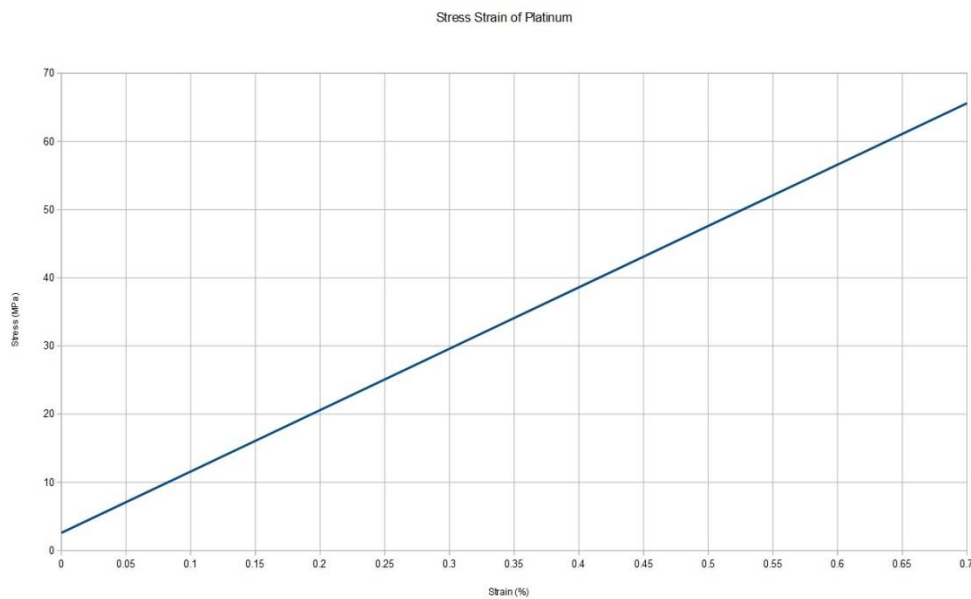
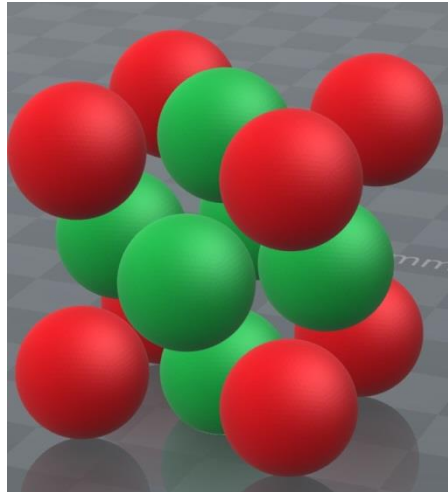


Figure 18 - Stress-strain behaviour of platinum derived from Koh et.al. experiments

## 2.3. FCC Materials

In order to get an idea of the crack and fracture behaviour of platinum, a 0.64mm thick copper wire was used. In addition to being cheaper, the thicker copper is much easier to work with. Platinum is a face centred cubic material (FCC). This is a material that has a cubic shape with a platinum atom at each corner of a cube and one on each face. Below is a representation of an FCC unit cell. The red spheres represent the corner atoms and the green spheres are the atoms on the face of the cell.



*Figure 19 - Unit cell of an FCC material*

The fact that platinum is an FCC material is important because it is a close packed system. One of the consequences of close packing is that the preferred slip systems are not temperature dependent, so in theory the temperature at which stress is applied does not have a bearing on the slip system that a dislocation moves along. This is because the directions that the atoms can move in during dislocation all require the same amount of energy. This also means that there is no ductile to brittle transition temperature like some body centred cubic materials (BCC).

FCC materials have 12 slip systems from 4  $\{111\}$  planes each with 3  $\langle 110 \rangle$  directions. The image below illustrates this slip using one of the  $\{111\}$  planes. The purple atom rests on top of one of these plane and can slip between the atoms above and below it in the  $\langle 110 \rangle$  directions.

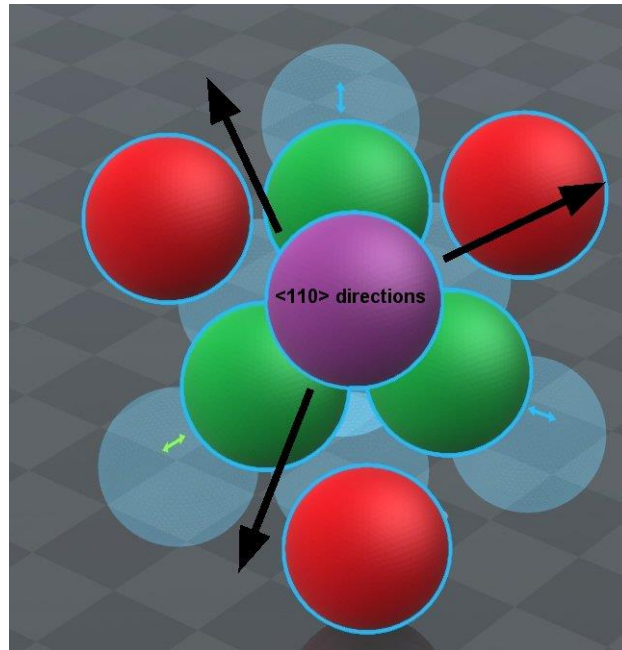


Figure 20 -  $\langle 110 \rangle$  slip directions

Dislocation movement occurs along the slip planes. This is because atomic movement along slip planes requires relatively low amounts of energy. The way that slip occurs is when an applied stress causes bonds around a dislocation to reform and shift said dislocation. Below is an example of the movement of an edge dislocation.

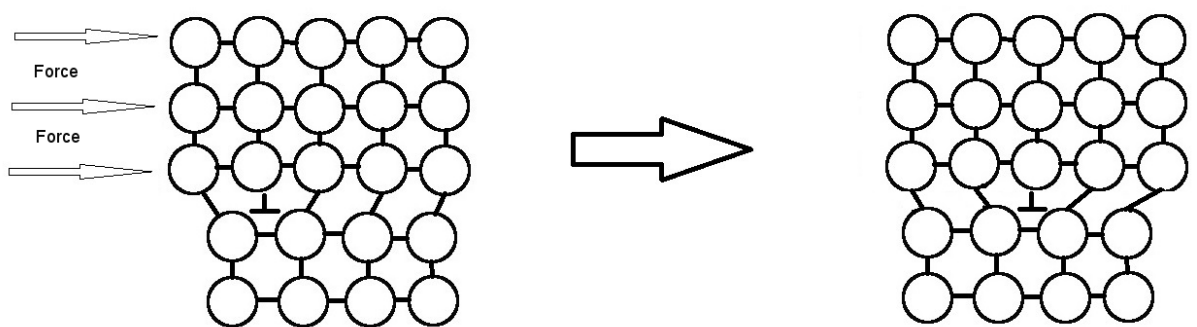


Figure 21- Model illustrating one form of dislocation movement (edge dislocation)

These slip planes are constant in all FCC materials which means that similar behaviour is expected between materials such as platinum and copper. Because of this, initial trials and setup with copper was done to get a preliminary model of how crack initiation, propagation, and eventual fracture would occur in platinum.

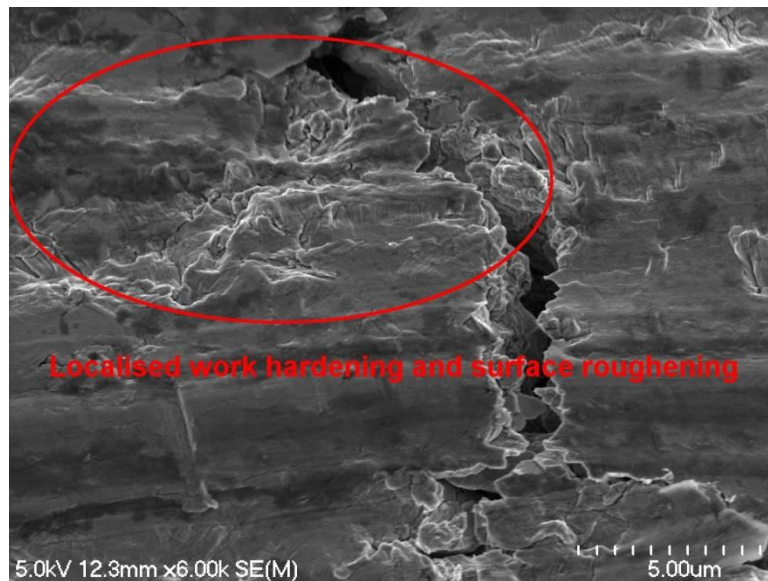
## **2.4. Fatigue Mechanics**

Fatigue is characterised by three major phases. Crack initiation, crack propagation, and failure. The general mechanism by which each phase progresses is by forward and reverse loading. The loading introduces defects that accumulate within the material that evolve into cracks after sufficient defects pile up together. These cracks then grow with each cycle until they grow to a critical size where the material fractures.

### **2.4.1. Crack Initiation**

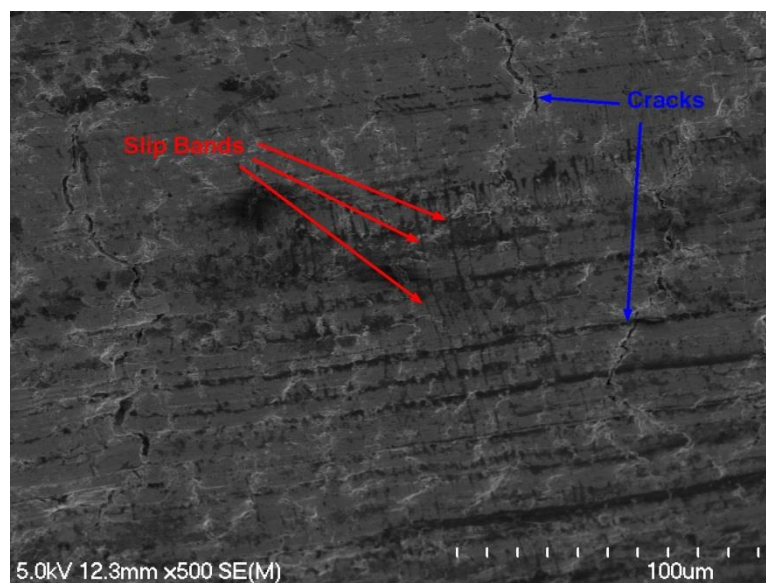
Fatigue is characterised by loading and unloading in a single direction. This causes dislocations to form in a preferred orientation. These dislocations are able to glide along slip planes that were described previously. The slip continues until the dislocation encounters an obstacle such as another, differently oriented, dislocation, grain boundary, or is pinned by a point defect such as an inclusion.

Subsequent dislocations form in the same manner and glide in the same way and are stopped at the same points. These dislocations stack up and form what is called a persistent slip band (PSB). This is an area of high strain concentration. The high volume of dislocations can cross-slip and climb which introduces vacancies, localised work hardening, and surface roughening.



*Figure 22 - Micrograph of a micro crack in copper*

After enough stress is applied, and enough dislocations are stacked on top of each other, these slip bands can break open and form what is known as a crack.



*Figure 23- Slip bands formed in a fatigued copper sample*

When a platinum sample that was fatigued for 5,000 cycles was put into the SEM, cracks started to be apparent in the surface of the sample on the order of

1 micron in size. These small cracks were used as initial crack sizes for further analysis. When samples were less fatigued, the surface was not obviously cracked.

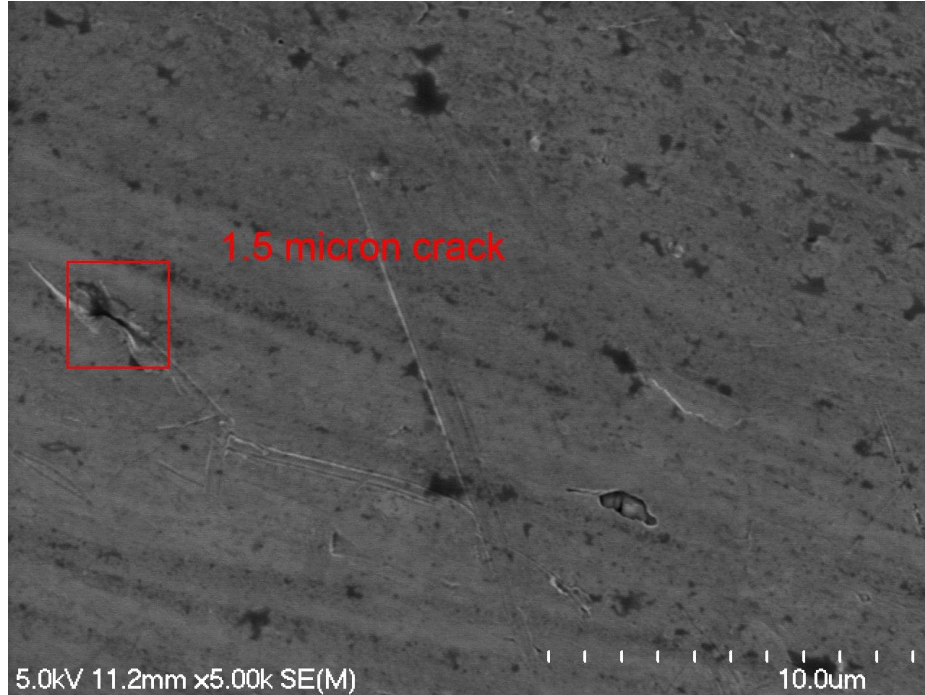


Figure 24- 5,000 fatigue cycle platinum sample showing crack initiation. 1.5 micron was the largest crack found

### 2.4.2. Crack Propagation

Once a crack has been initiated, it grows at a rate related to the applied stress for each cycle. This behaviour is described by Paris' law.

$$\frac{da}{dN} = C(\Delta K)^m$$

$C$  and  $m$  are material constants

$$\Delta K = Y\sqrt{\pi a} \times (\sigma_{max} - \sigma_{min})$$

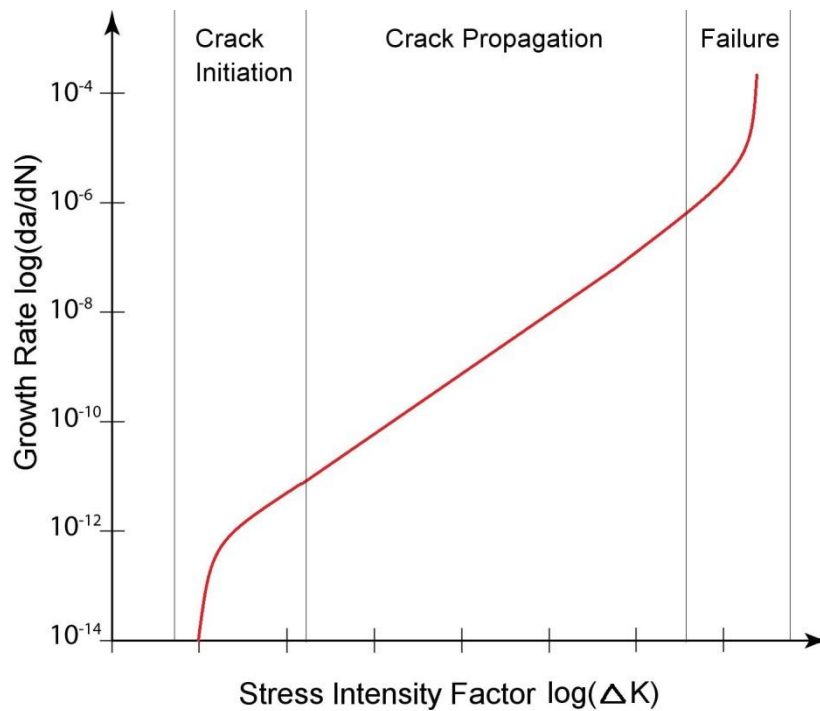
$a$  is the crack length

$Y$  is a geometry factor

This shows that the crack growth accelerates with each cycle. The initial crack size used in platinum crack propagation analysis was 1 micron in order to



get an order of magnitude idea of how many cycles were needed for failure. The material constant  $m$  is dimensionless and generally between 3 and 5. The  $C$  value is a little bit trickier and needs to be experimentally determined. It generally varies from  $10^{-7}$  to  $10^{-12}$  MPa and is highly dependent on material, grain structure, and material phase. When the crack growth is plotted in a log-log plot, it has a general shape shown below.

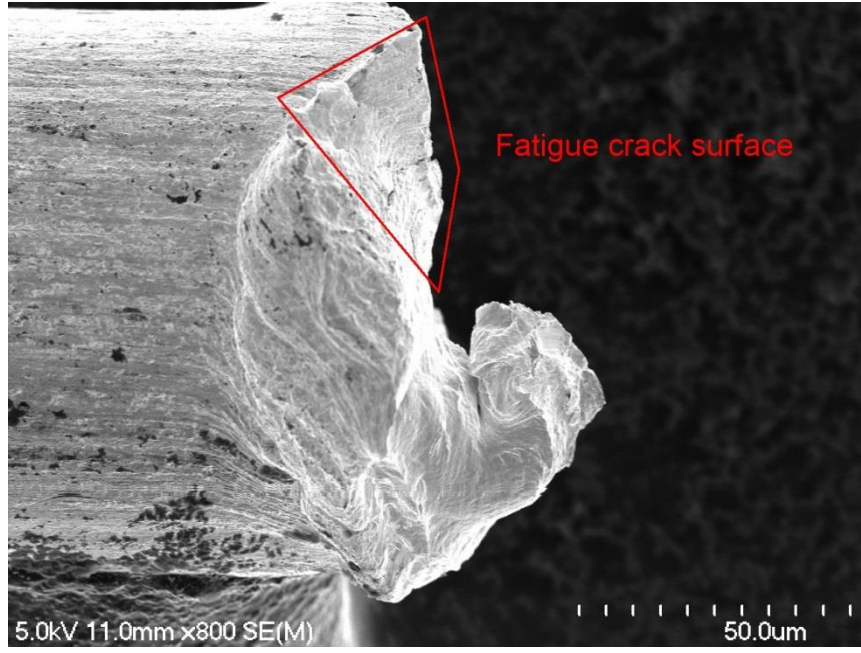


*Figure 25- Typical behaviour of fatigue cracking. Log-log plot*

### 2.4.3. Failure

Once a crack has grown to a critical crack size, the material will fracture. This crack size is dependent on the material, its microstructure, and the applied load. The critical crack size for the platinum wire used has to be experimentally determined. In order to do this, a test was run until the material failed and a micrograph was taken to look at the fracture surface.





*Figure 26- Ductile failure of a fatigued platinum wire sample*

In platinum, the critical crack size was determined to be about 35 microns when a load of about 50MPa is applied. This then can be converted into a number of cycles to fatigue failure using a life estimation version of Paris law.

$$N_f = \int_{a_0}^{a_c} \left[ C (\Delta \sigma Y \sqrt{\pi})^m a^{m/2} \right]^{-1} da$$

## 2.5. Mathematical Model

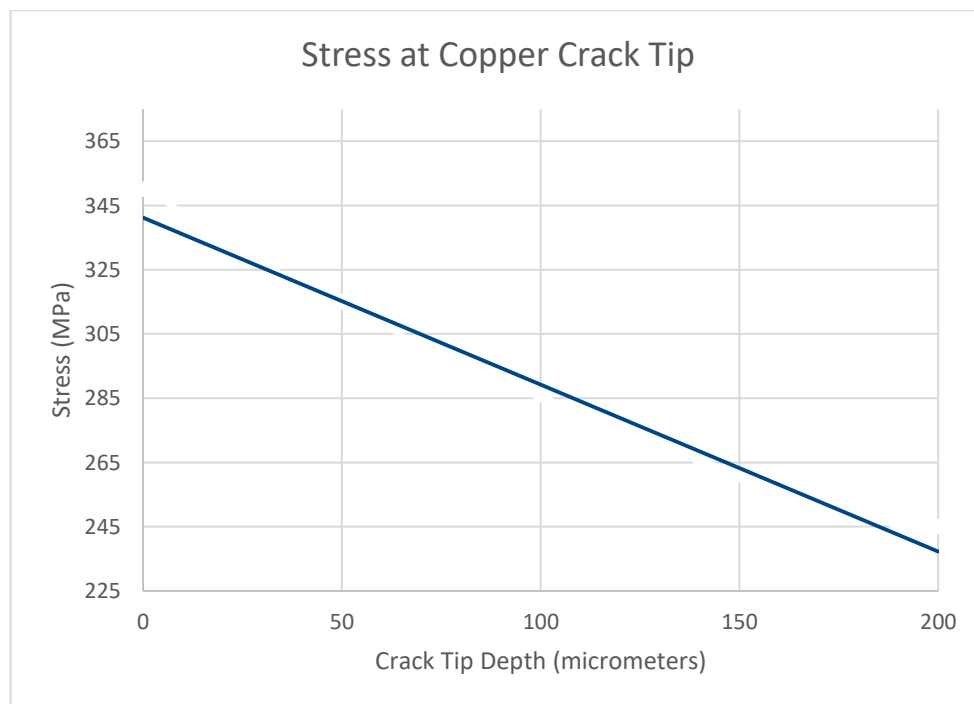
A mathematical model was first built in order to predict a crack size vs. number of fatigue cycles. Integrating the life estimation of Paris' law yields

$$N_f = \frac{a_c^{1-m/2} - a_0^{1-m/2}}{C (\Delta \sigma Y \sqrt{\pi})^m (1 - m/2)}$$

The first task was to get a rough estimate of how many cycles are needed to fracture the 640 micron in diameter copper wire in order to determine if Paris' Law is applicable in this situation. Micrographs of fractured samples showed that the critical crack length of this copper wire is approximately 200 microns when a 0.5 bending strain is applied. The initial crack length was on the order of 10 microns. Then the values for  $m$  and  $C$  from a fracture mechanics text book<sup>(9)</sup> were taken. The geometric factor,  $Y$ , was calculating by assuming pure bending at any instantaneous moment<sup>(14)</sup>.

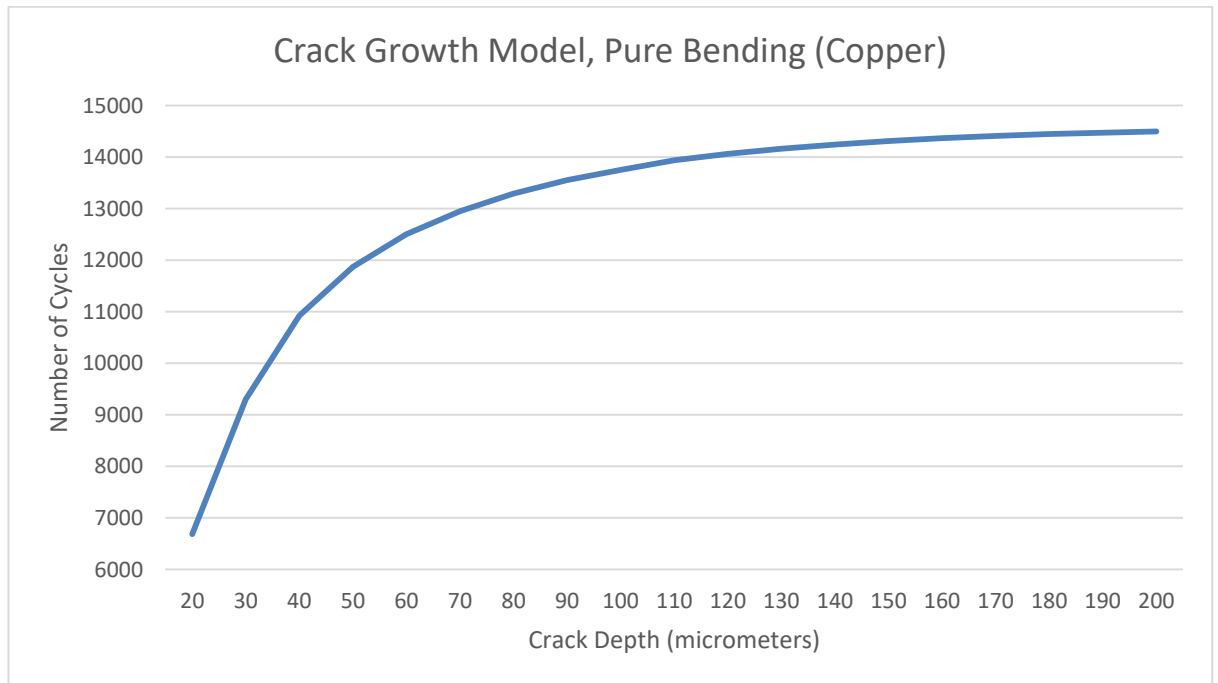
An important consideration is the nature of the applied stress. Pure bending means that the more the crack approaches the neutral axis, the less strain (and therefore stress) is applied to the crack tip. This means that as the crack grows, less stress is acting to grow the crack.

The stress that is applied to the wire at each depth can be plotted using the stress/strain behaviour of the material mapped to the strain at the distance from the neutral axis in a sample undergoing pure bending.



*Figure 27 - Model of stress at crack tip in the copper wire*

Then using the Paris model, the following crack behaviour can be expected.



*Figure 28 - Crack tip depth for copper at 0.5% strain cycles*

A similar kind of model can be made for the platinum wire. This shows a much more linear behaviour because of the size of the wire. The small diameter means that as the crack grows, the tip reaches the neutral axis very quickly. This causes the amount of strain, and therefore stress, to drop off very quickly which offsets the exponential growth rate. In addition, pure bending has a different effect than plain tensile stresses on the geometric factor,  $Y$ .

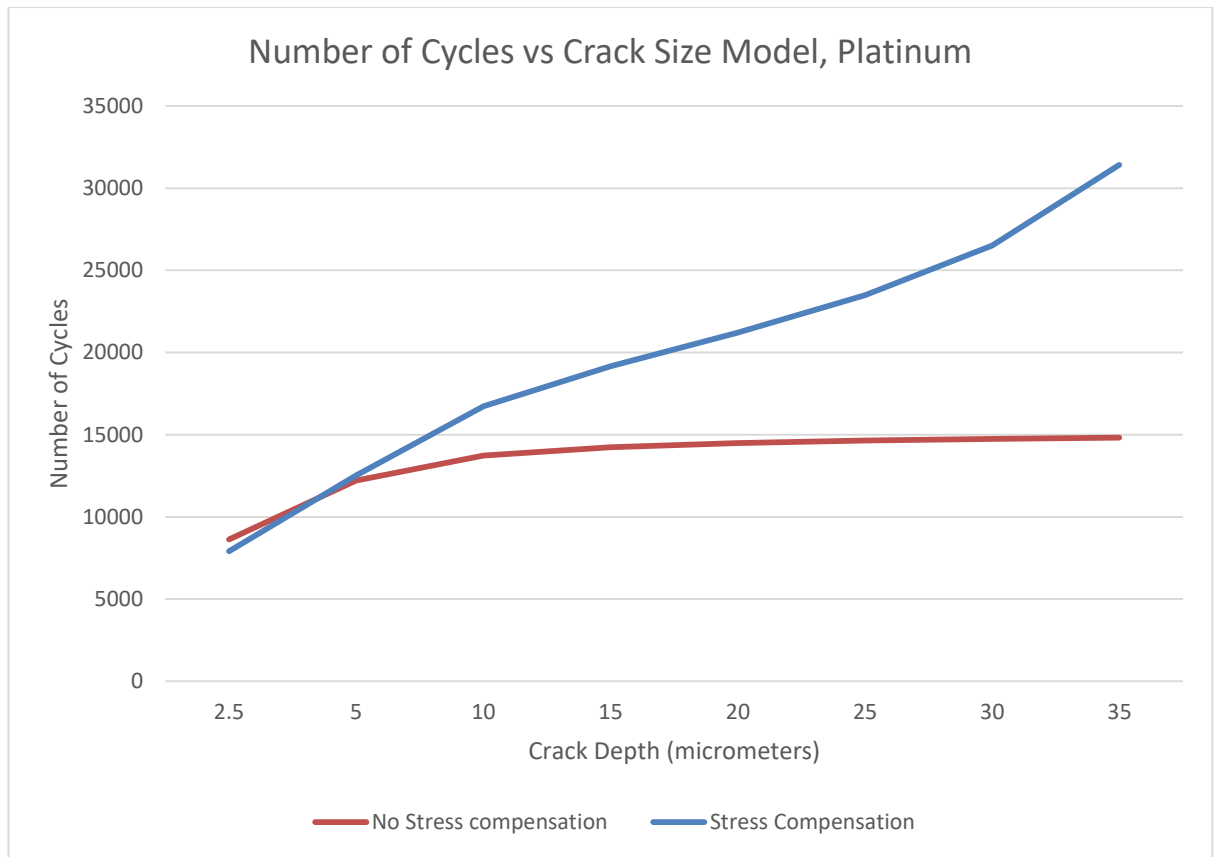


Figure 29- Crack tip depth for platinum at 0.5% strain cycles

## 2.6. Experimental Setup

In order to fatigue test such a thin sample, traditional fatigue setups are not viable. Fatigue is generally tested on large samples meant for structural applications. This is done by applying a large transverse load onto a sample. For a wire that is not meant to bear a load in this manner, the other two options are ultrasonic fatigue testing and rotating fatigue testing.

Ultrasonic fatigue testing has the advantage of being able to fatigue a much larger area of a sample more quickly. This method, however, has the drawback of being more complicated to build in a way where the stress/strain can be controlled. For this reason, to study the mechanics of fatiguing in this platinum wire, rotational fatigue was chosen.

## 2.7. Rotational Fatigue

The way that rotational fatigue works is by rotating a sample while it is bent around a fixed circular radius. This causes the inside of the wire to experience compression while the outside experiences tension. As the sample is rotated, the surface transitions from a state of compression to tension with each rotation. The amount of strain applied can be derived from the radius of the wire and the radius the wire is bent around.

$L$  = length of the wire (neutral axis length)

$d$  = wire diameter

$L_t$  = length of the outside of the wire (under tension)

$R$  = radius of curvature (neutral axis)

$R_t$  = radius of curvature for the wire under tension

$\varepsilon_t$  = strain of the wire under tension

$$R_t = R + \frac{d}{2}$$

$$\varepsilon_t = \frac{L_t - L}{L} = \frac{2\pi R_t - 2\pi R}{2\pi R} = \frac{R_t - R}{R} = \frac{d}{2R}$$

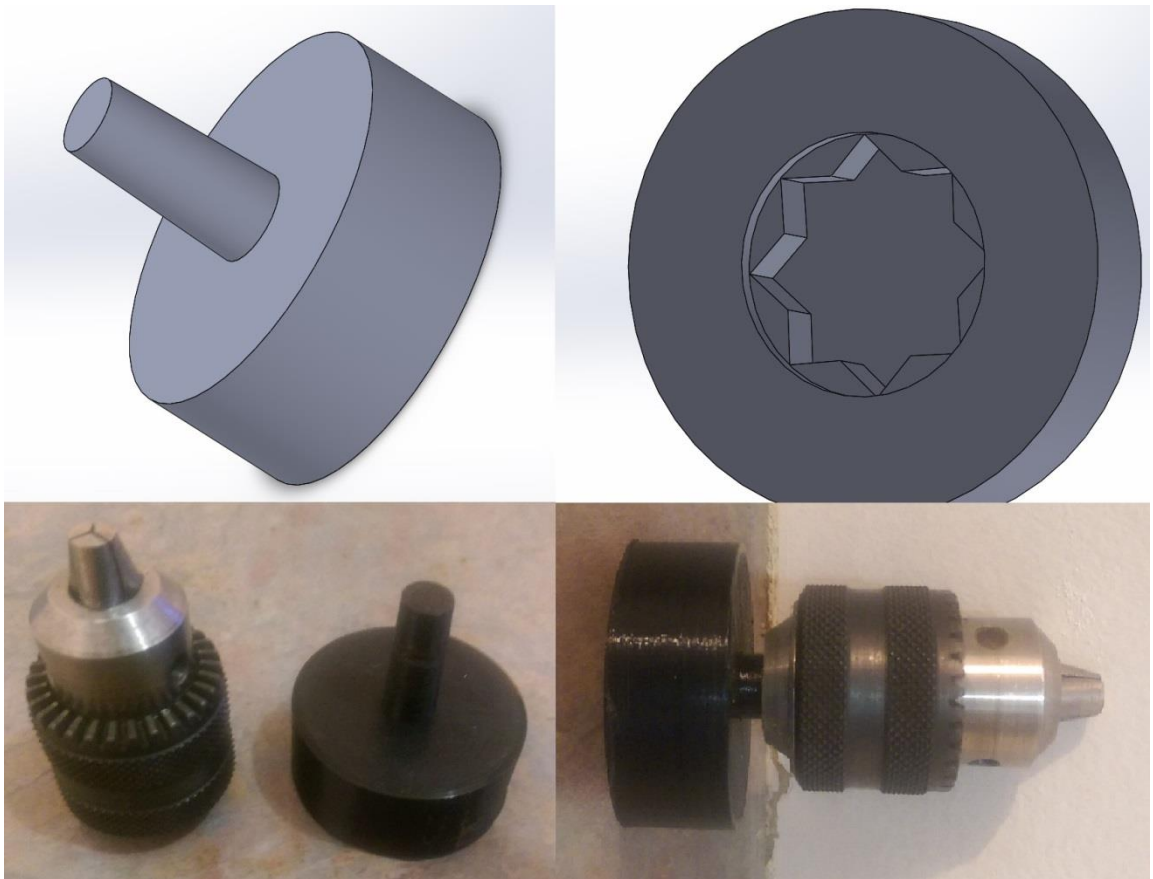
If the chosen stress is to be just under 50 MPa the strain needed is 0.5% <sup>(9)</sup>. Inserting this into the above equation with the diameter of the wire (100  $\mu\text{m}$ ), the radius of curvature needs to be 10mm.

## 2.8. Test Rig Design

The experimental setup required three major parts. The first is a motor that is capable of turning at a constant speed for hundreds of hours at a time. A 12V DC motor that drives a car window was found and chosen to drive the rotating

wire. This motor rotates at 1.4 rotations per second. This is a little slow, but the fatigue limit is on the order of  $10^4$  rotations, so any test in this order of magnitude can be completed in a few days. A motor that rotates more quickly can be used but is less reliable unless it is an AC motor.

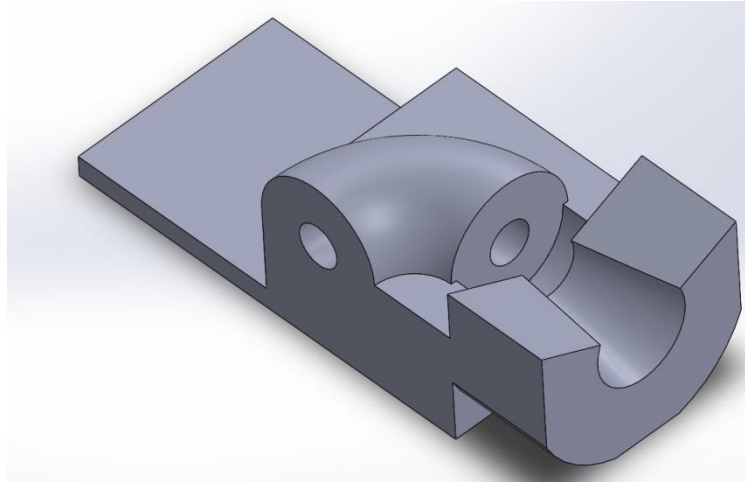
The second part needed is a way to hold the wire. To do this, a high quality drill chuck was found. This drill chuck needed to have the ability to clamp down to 0mm in order to hold a 100 micron wire. An LFA 0-1/4" drill chuck was acquired and found to be able to hold this wire securely. To be able to mount the drill chuck to the motor, a mount was designed in Solid Works and 3D printed.



*Figure 30- Drill chuck stand for mounting onto a DC motor, design and the printed part*

The final piece needed is a way to hold in a bent shape around a fixed radius. The way this is generally done is around a cylindrical structure. The size and stiffness of the platinum wire did not allow this, so a different approach was

needed. A tube that is bent with the desired radius was used instead. This was also designed in Solid Works and 3D printed.



*Figure 31- Stand to hold a wire in a constant bend*

When the test rig is set up, the motor rotates at a constant speed for even extended periods. Run times up to 10 days of continuous operation were completed to test the reliability of the motor and rig as well as to make sure that the motor continued to rotate at a constant speed. The final setup worked without failure for all the tests of both copper and platinum samples.

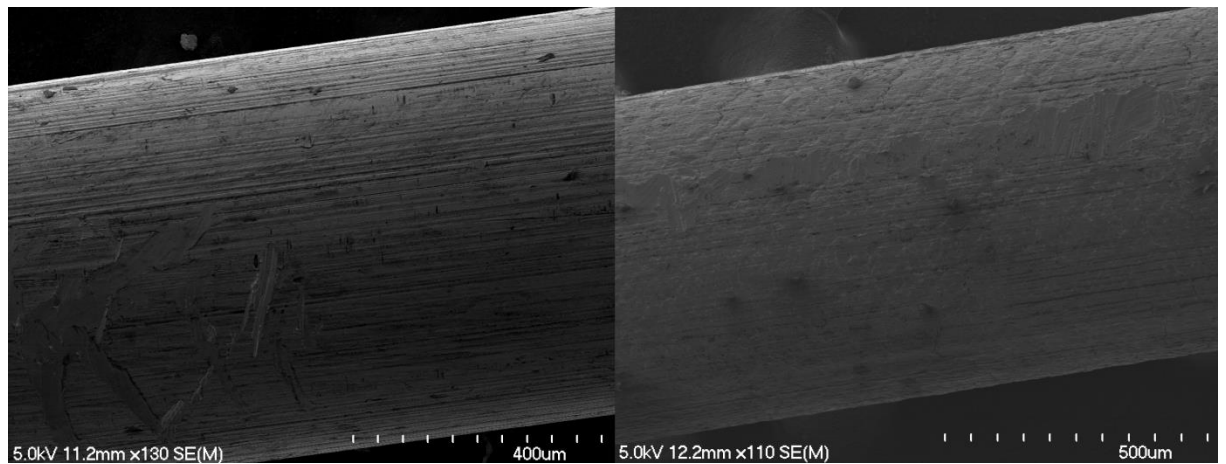


*Figure 32- Test fixture when assembled*

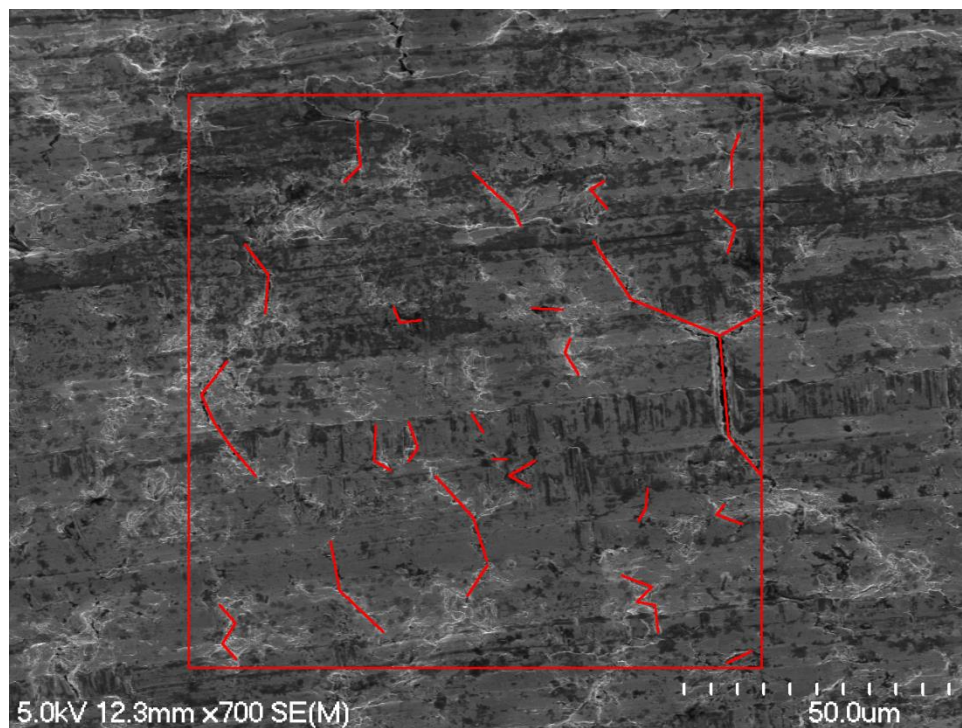
## **2.9. Results, Copper**

Surface texture of copper after fatiguing was dramatically altered. This is because of the high amount of dislocations and the cracks that accumulate on the surface. The crack density measured was approximately  $3\mu\text{m}/100\mu\text{m}^2$  in a sample that was fatigued to failure. This is done by measuring the total length of cracks in a known area.





*Figure 33 - Copper wire before (left) and after (right) fatigue*

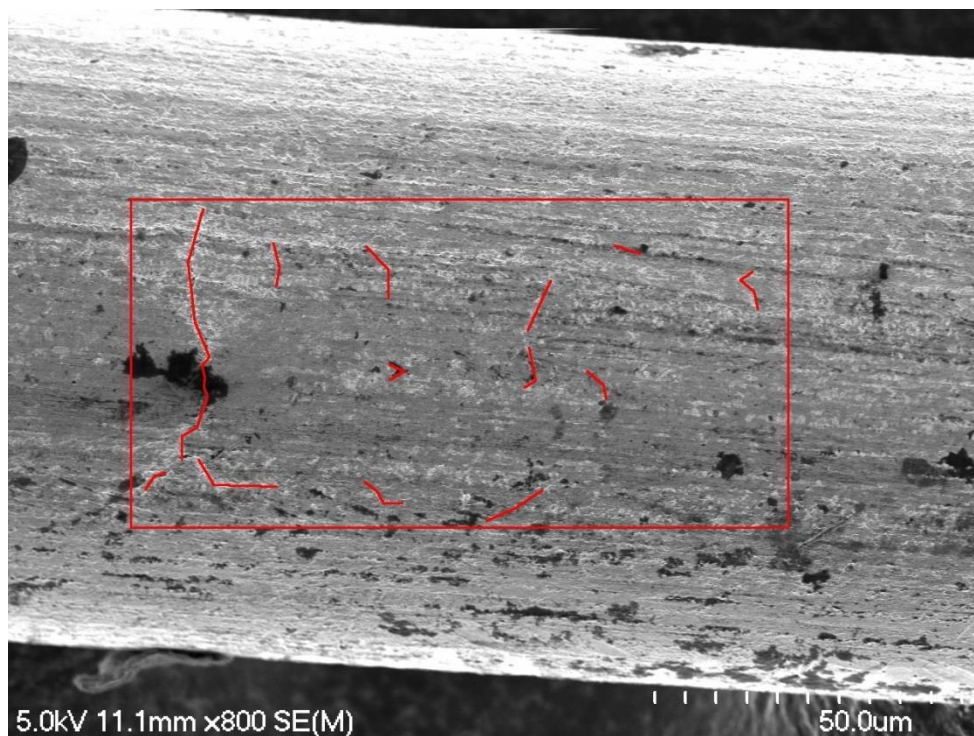


*Figure 34- Copper surface after fatigue to failure*

Copper wire was tested to failure 3 times and the number of cycles recorded. These samples fractured at an average of 14,900 cycles. This lines up very closely with the model prediction of 14,500 cycles.

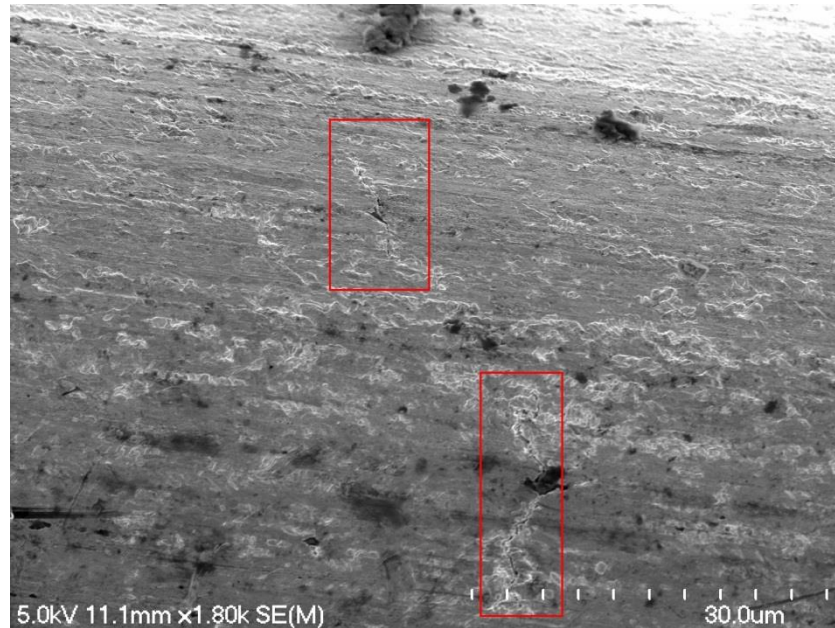
## 2.10. Results, Platinum

A closer and more comprehensive look was taken at platinum. The crack density was calculated over several areas that were fatigued. The average was found to be about  $2.5\mu\text{m}/100\mu\text{m}^2$  in a sample that was fatigued to failure.



*Figure 35- Platinum surface of a sample fatigued to failure*

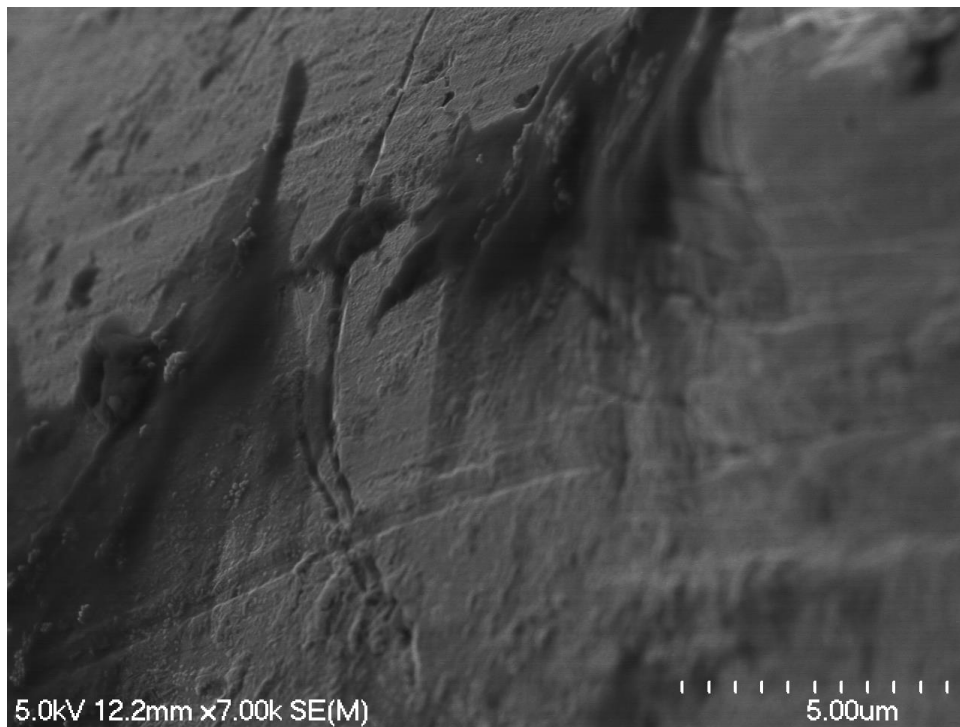
Samples that were run to failure took 31,000 and 32,500 cycles to fail. Two samples underwent 5,000 cycles to look for initial crack sizes. Sets of three tests were done at 7,000, 10,000, 15,000, 20,000, and 25,000 cycles. For analysis, each of the samples had several of the larger cracks measured and averaged in order to determine a crack length.



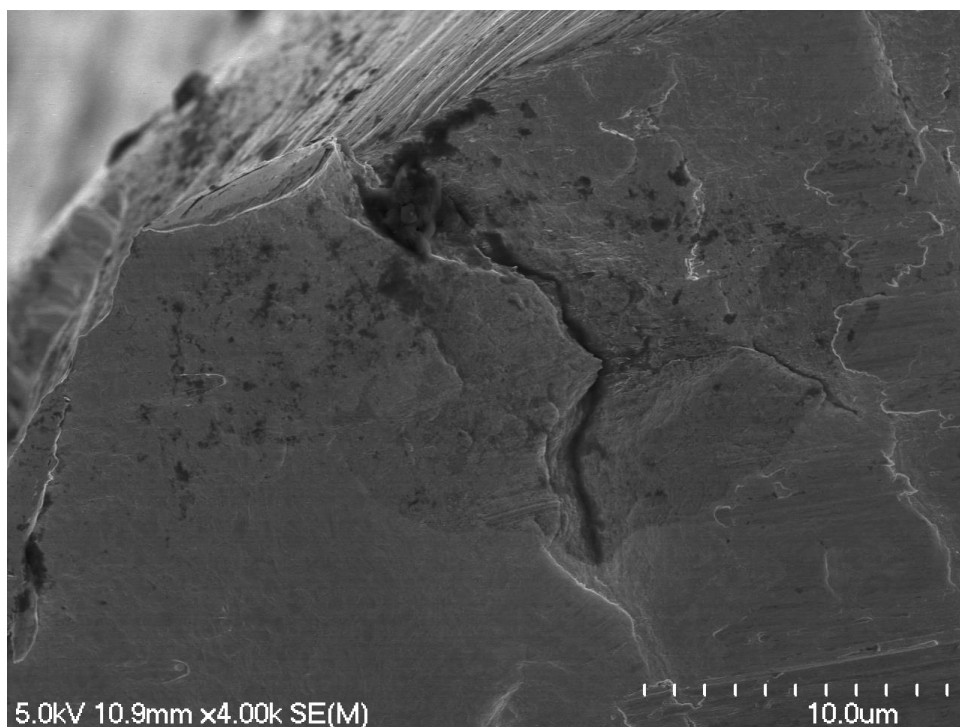
*Figure 36- Example of cracks used for size analysis*

Cross sections of the wires were taken to measure crack depth as well as surface pictures to measure crack length. These measurements showed that the length and depth of any given crack was about the same. This is seen nicely in a sample fatigued to with 20,000 cycles. Below are pictures of both a cross section and a surface crack of the same sample. Both show a crack size of about 15 microns.



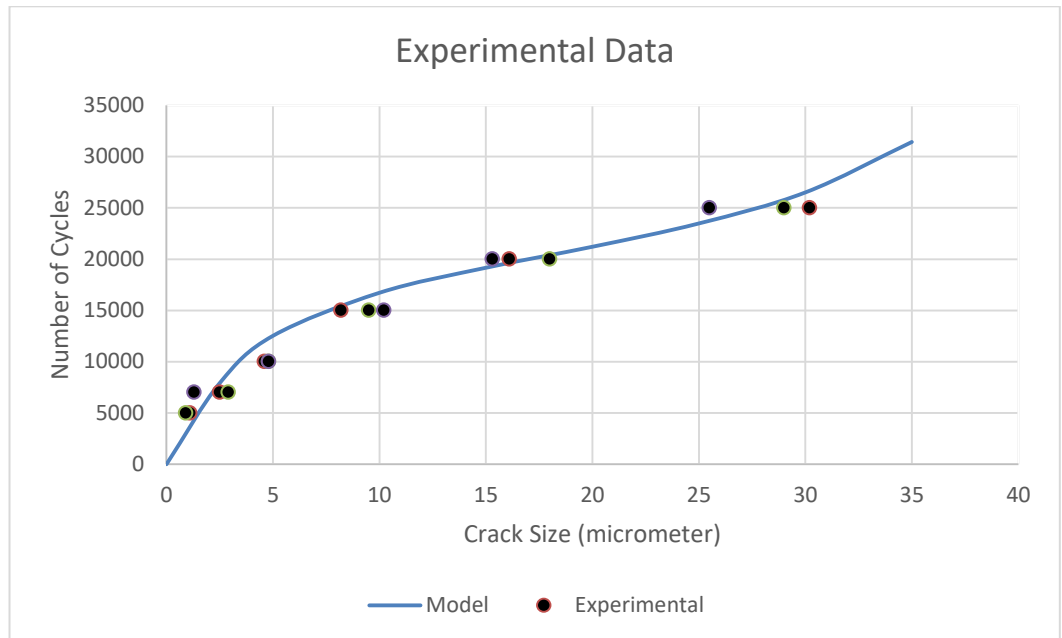


*Figure 37- Single large crack in 20,000 cycle sample*



*Figure 38- Cross section of a crack in a 20,000 cycle fatigue platinum wire*

The crack sizes were found to vary from 1 to about 35 microns. The cracks generally seemed to grow in a way that reflected the mathematical model. The results are graphed along with the mathematical model.



*Figure 39 - Experimental data plotted on the crack growth model*

### 3. Discussion of Results

The goal of this study was to determine if there is a reliable way to increase the surface roughness of a thin platinum wire. The surface roughness has to penetrate at least 10 micro meters into the sample and be consistent throughout the wire. This section discusses the results of the Otten method and the rotary fatigue method and their applicability in surface roughening.

### 3.1. Ottenisation

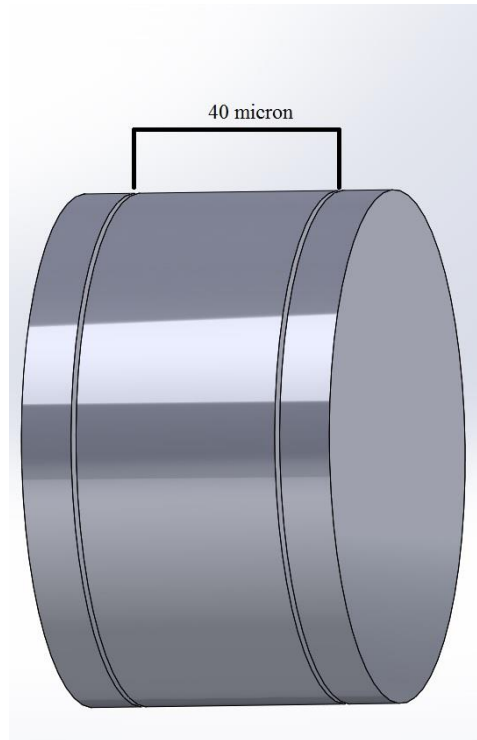
The Ottenisation method created a surface that was extremely porous. The pores ranged in size from 0.25 microns in diameter to 1 micron in diameter as can be seen in figure 13. Changing the parameters of the treatment drastically changes the surface morphology of the sample. This may be a limitation to this method.

In addition, the depth of treatment is extremely limited with this type of treatment. The source of platinum is the surface of the wire itself. Therefore, as the surface becomes completely covered in porous platinum, the solid platinum underneath stops being a source of material and the treatment becomes redundant. The tests done have shown that this maximum depth of treatment is between 1.5 and 2 microns deep.

In order to make a thick layer of porous material, deposition may be used, but an outside source of platinum is needed. A method that can be tested is to use a platinum salt such as platinum(II)chloride dissolved in solution. This would then be deposited using a pulsed (or continuous) bias on the platinum wire. The wire would have to undergo hydroxide reduction in a similar manner to what was carried out in the Ottenisation treatment.

### 3.2. Mechanical Fatigue

Mechanical fatigue creates surface defects that grow predictably and have a statistically regular density of formation. When crack depths (sizes) of approximately  $15\mu\text{m}$  were reached, the density was about  $2.5\mu\text{m}/100\mu\text{m}^2$ . This translates to a crack that travels the entire circumference every  $40\mu\text{m}$  for the  $100\mu\text{m}$  thick wire, as illustrated in figure 40. However, this is a statistical interpretation, and the reality is that the cracks do not form in this way.



*Figure 40 - Statistical interpretation of crack density*

This regularity cannot be directly controlled since the areas where persistent slip bands form is dependent on factors at the atomic level. For the samples tested, the crack initiation density varied between 1 crack per  $12,500\mu\text{m}^2$  and 1 crack per  $25,000\mu\text{m}^2$ . This means that for a length of wire 1mm long, the number of cracks that can be expected to initiate is between 10 and 25. This is for a wire with a grain size of  $1\mu\text{m}^2$ .

If the grains were to be made smaller it would raise the number of grains per unit area. This should increase places for dislocations to pin thus increasing the crack density. This should be tested using different wires with different grain sizes. It is important to note that changing grain sizes has an effect on mechanical properties. This means that the tensile strength, crack growth rate, and number of cycles to failure changes.

On the other hand, the crack depth can be mostly regulated. For this particular wire the cracks reached a depth of 15 microns after just under 20,000 cycles at 0.5% strain. Different depths can be reached with repeatability depending on the initial quality of the wire to be fatigued.

The crack growth rate increases with each cycle. This makes controlling cracks delicate. Any imperfections or pre-existing cracks are points of accelerated failure when fatiguing a sample. This is more and more apparent as the cracks grow. The experimental result showed that as the sample underwent more cycles, the variability in crack size also increased (figure 39).

Fatiguing a sample by pure bending compensates for this by decreasing the amount of stress on the crack tip as it grows. This has the disadvantage of being difficult to do over the entire length of a thin wire. Because of the nature of rotational fatigue, only about 2-3 centimetres of wire can be fatigued at a time.

One solution to this is by crack with ultrasonic fatiguing. This is where a length of wire is fixed at both ends with a nominal load applied. Then an ultrasonic vibration is applied to a wire end at a known frequency. This has the advantage of being able to treat a long length of wire much more quickly and energetically efficiently than rotational fatigue. The disadvantage is that the applied load is much more difficult to control.

In addition, the type of mechanical loading becomes pure tensile stress verses the pure bending or rotational fatigue. This means that the increasing crack growth rate is no longer offset by decreasing load on the crack tip. The resulting crack growth would be expected to follow more closely with the uncompensated growth model in figure 29. The increasing growth per cycle would make controlling the cracking more difficult but likely possible depending on the wire. If the wire is of very high quality: constant grain sizes and relatively free of defects at the surface, fatigue may be a viable method to induce surface cracks of desired depth.



## References

1. PLATINUM 10% IRIIDIUM MATERIAL #: 100167. *California Fine Wire Company*. [Online] <http://www.calfinewire.com/datasheets/100167-platinum10iridium.html>.
2. **Getzlaff, Mathias**. *Fundamentals of Magnetism*. Berlin : Springer-Verlag, 2008.
3. **Buxton, Richard B**. *Introduction to Functional Magnetic Resonance Imaging*. Cambridge : Cambridge University Press, 2009.
4. *Growth modes of platinum overlayers resulting from square wave perturbing potential treatments of different symmetries*. **Visintin, A, et al., et al.** 1989, Journal of Electroanal. Chem, pp. 191-205.
5. **Lide, David R**. *Handbook of Chemistry and Physics*. s.l. : CRC Press, 2003.
6. *Electrochemical corrosion of platinum electrode in concentrated sulfuric acid*. **Fumihiko Koderu, Yu Kuwahara, Akira Nakazawa, Minoru Umeda**. 2007, Journal of Power Sources, pp. 698-703.
7. **Bard, A J**. *Encyclopedia of Electrochemistry of the Elements Vol. VI*. New York : Marcel Dekker, 1976.
8. **Otten, Josephus M**. 5,326,448 United States/Florida, 1994.
9. **Maiti, Surjya Kumar**. *Fracture Mechanics*. Delhi : Cambridge University Press, 2015.
10. Platinum. *ESPI Metals*. [Online] <http://www.espimetals.com/index.php/technical-data/186-Platinum>.
11. Platinum (Pt) Wire Material Information. *GoodFellow*. [Online] <http://www.goodfellow.com/E/Platinum-Wire.html>.
12. Platinum. *MATBASE*. [Online] <https://www.matbase.com/material-categories/metals/non-ferrous-metals/other-non-ferrous-metals/material-properties-of-platinum.html>.
13. *Molecular dynamics simulation of a solid platinum nanowire under uniaxial tensile strain: Temperature and strain-rate effects*. **Koh, S J, et al., et al.** 2005, Physical Review, pp. 2-11.
14. **Tada, Hiroshi, Paris, Paul C and Irwin, George R**. *The Stress Analysis of Cracks Handbook Third Edition*. s.l. : ASME, 2000.
15. **Kundu, Tribikram**. *Fundamentals of Fracture Mechanics*. Boca Raton : CRC Press, 2008.
16. **Jones, Denny A**. *Principles and Prevention of Corrosion Second Edition*. Upper Saddle River : Prentice Hall, 1992.
17. *The Resistance to Fatigue Crack Growth of the Platinum Metals*. **Speidel, Markus O**. 1981, Platinum Metals Review , pp. 24-31.

18. *Mechanics of Surface Roughening in Metal Forming Process*. **Wilson, William R.D. and Lee, Weiming**. 2001, Journal of Manufacturing Science and Engineering, pp. 279-283.
19. *The physics of Fatigue Crack Initiation*. **Sangid, Michael D**. 2012, International Journal of Fatigue .
20. *Synthesis of Porous Platinum Nanoparticles*. **Teng, Xiaowei, et al., et al**. 2006, Small Journal, pp. 249-253.
21. *Formation and Evolution of Persistent Slip Bands in Metals*. **Trochidis, A, Douka, E and Polyzos, B**. 2000, Journal of the Mechanics and Physics of Solids, pp. 1761-1775.
22. *Stress and Strain States in a Pseudoelastic Wire Subjected to Bending Rotation*. **Wagner, Martin F.X. and Eggeler, Gunther**. 2006, Mechanics of Materials, pp. 1012-1025.
23. **Materials, AZO**. Platinum - Exploration and Extraction. *AZO Materials*. [Online] <http://www.azom.com/properties.aspx?ArticleID=1345>.
24. *Strategies for the Fabrication of Porous Platinum Electrodes*. **Kloke, Arne, et al., et al**. Freiburg : Advanced Materials, 2011, Vol. 23.

## Appendix A Current Density Calculation

Electrons needed to ionise a monolayer of platinum wire. (001) plane orientation at the surface of pure platinum was assumed at all points.

$r$  = radius of the wire

$L$  = length of the wire

All calculations done in base units (meters)

$$S.A. = \pi r^2 + 2\pi rL$$

$$r = 5 \times 10^{-5} m$$

$$L = 0.1 m$$

$$S.A. = 3.14 \times 10^{-5} m^2$$

FCC structure with a lattice parameter of 3.91 Å. In the (001) plane, there are 2 atoms per unit cell.

$$\frac{2 \text{ atoms}}{1.5304 \times 10^{-19} m^2}$$

To calculate the number of atoms in the surface

$$3.14 \times 10^{-5} m^2 \times \frac{2 \text{ atoms}}{1.5304 \times 10^{-19} m^2} = 4.1 \times 10^{14} \text{ atoms}$$

Each platinum atom releases 2 electrons to become a  $Pt^{2+}$  ion

$$4.1 \times 10^{14} \text{ atoms} \times \frac{2e^-}{\text{atom}} = 8.2 \times 10^{14} e^-$$

1 Coulomb is  $6.242 \times 10^{18} e^-$

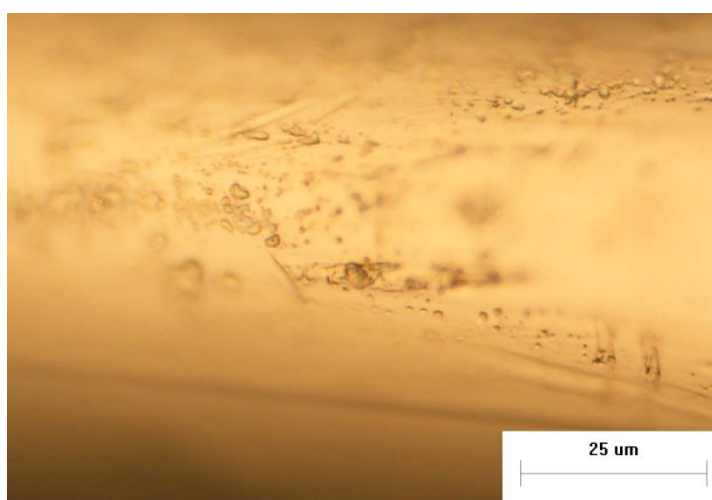
$$8.2 \times 10^{14} e^- \times \frac{1 C}{6.242 \times 10^{18} e^-} = 1.3 \times 10^{-4} C$$

Pulse length is 0.71ms or 0.00071s therefore current may be calculated.

$$\frac{1.3 \times 10^{-4} C}{.00071 s} = 0.190 A$$

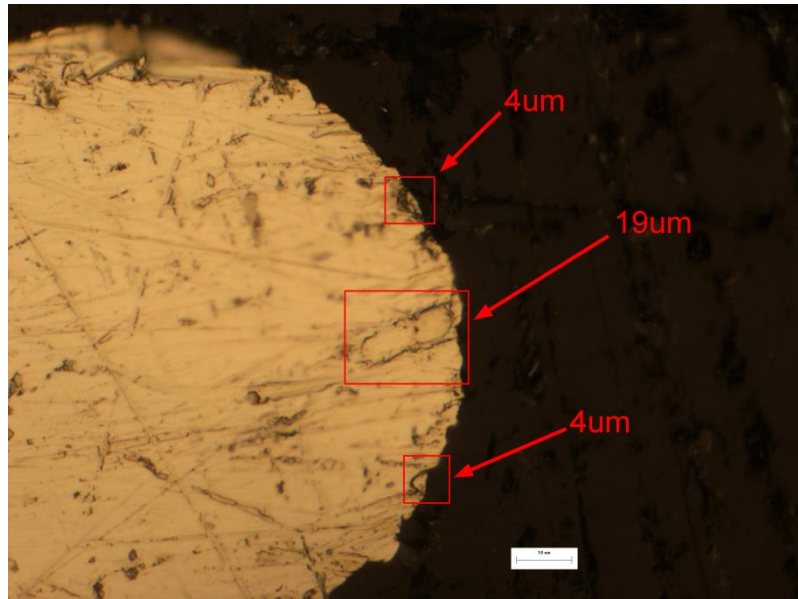
## Appendix B Pure Pitting of Platinum Wire

In order to increase the growth size and depth of the electrochemical treatment, a pure pitting experiment was conducted. After the Ottenisation was completed the high roughness was used as initiation points for pitting corrosion. The roughened wire was submerged in a stagnant 3 molar NaCl solution and given a +5V bias. This was left for 24 hours and observed in an optical microscope.



*Figure 41 - Pure pitting at the surface of a platinum wire*

The growth sizes in the Ottenisation-only process were under 1 micron as can be seen earlier in this paper. The pit sizes, when this corrosion step was added, varied from 1 micron to 5 microns in diameter. This can be controlled to be larger or smaller by adjusting the treatment duration. In addition to larger surface textures, the pores can be made much deeper. In the wire shown in figure 7, the pits were observed to reach a depth of 19 microns as seen below.



*Figure 42- Cross section of a pitted platinum wire sample*

Longer treatments increase pit size and depth but decreases regularity. The variability of pit size and depth increases as corrosion treatment time increases. A more detailed analysis of this variability will require the SEM. In addition, the total surface roughness seems to be lower than in an Ottenisation-only treatment. This was not studied in depth and would have to be confirmed with SEM imaging.